

DENSITY FUNCTIONAL THEORY OF LONG-RANGE
INTERMOLECULAR FORCES

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Bachelor of Science

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1982

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
Master of Science
May, 1986

Thesis
1986
M6976
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PREFACE

The Ground-State Energy of a system of two neutral molecules was developed using the formalism of Density Functional Theory. This method of approach in deriving the Ground-State Energy bypasses the traditional quantum mechanical wave function method and was seen to be considerably simplified in its computational procedures.

Using the formulation of Levy and Freed, the electron density, and then the Energy Functional, was obtained as a Taylor Series expansion about a reference density. Optimization of the density then led to the derivation of the Ground-State Energy when this optimum density was used as the density in the Energy Functional.

I am indebted to Dr. Paul Westhaus, my major adviser, who introduced me to the subject of Density Functional Theory and without whose invaluable help, concern and guidance I find it impossible to produce these pages.

I am also thankful to Dr. Larry Scott and Dr. George Dixon for serving as my committee members, as well as to other professors whose tutoring in Physics and Mathematics led to the understanding of the physical concepts displayed in this thesis.

I dedicate this work to my two sons Ahmad Abu Dhar and Abdullah Bakhtiar Junaidi.

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CHAPTER I

INTRODUCTION

The theoretical approach now known as Density Functional Theory has been popular for the last two decades in the realm of molecular physics due to its predictive and interpretative formulations of the forces in molecules and molecular systems. This approach is appealing because it holds the promise of conceptual as well as computational simplifications as it attempts to derive, without resorting to the traditional wavefunction method, the total electronic energy of systems within the context of potential energy surfaces. The knowledge of such systems is very important because it can help us to understand a lot about macroscopic phenomena.

For example, if the nuclei are arranged on a periodic lattice, we can predict the lattice vibrational (phonon) spectrum of the solid by slightly distorting the lattice and recalculating the ground state electronic energy as a function of the distortion. Knowing this allows us to evaluate optical, thermal and magnetic properties of the solid. We can also write down the equation of state, electron density distributions and cohesive energy of such a solid all of which can be verified by experiments. And when phonon and electron properties of a metal are investigated together, one can calculate its superconducting transition temperature.

Density Functional Theory provides a systematic approach with which one can obtain the energies necessary to observe and predict all of the phenomena described above. We can use the theory to derive interaction energies that in turn produce potential energy surfaces that fit well with experimental results. The energy of interaction of two or more molecular fragments is defined as the total electronic energy of the system with the nuclei of all the atoms fixed in place plus the Coulombic repulsion energy of the nuclei. Here, by "molecular fragments" we mean a collection of nuclei whose internal coordinates do not change during the course of our considerations. Of course, we shall want to obtain the interaction energy as these fragments assume different spatial arrangements vis a' vis each other.

The electronic energy of each fragment (including the nuclear repulsion energy) computed for the isolated fragment, is then subtracted to define the potential energy of interaction for that configuration of the fragments. A plot of such potential energy of interaction in terms of all the coordinates which are allowed to change as the fragments assume various positions relative to one another constitutes the potential energy surface. The focus of the problem, point by point on the potential energy surface, is then finding the total electronic energy of the interacting fragments. This then is the motivation for Density Functional Theory.

In general, let us consider F fragments indexed $f = 1, 2, 3, \dots, F$. The f th fragment has A_f nuclei and thus $3A_f$ nuclear coordinates. In turn, these may be divided into two sets; six "external" coordinates \vec{R}_f and Ω_f which are the center of mass and the Euler angles, respectively and $3A_f - 6$ "internal" coordinates which we will write as $\{\vec{\tau}_f\}$.

The Hamiltonian can be written quite generally as

$$\begin{aligned}
 H = & \sum_{i=1}^F \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{f=1}^F \sum_{a_f=1}^{A_f} \frac{-Z_{a_f} e^2}{|\vec{r}_i - \vec{R}_{a_f}|} \right\} + \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \\
 & \sum_{1 < f < f' < F} \sum_{a_f=1}^{A_f} \sum_{a_{f'}=1}^{A_{f'}} \frac{Z_{a_f} Z_{a_{f'}} e^2}{|\vec{R}_{a_f} - \vec{R}_{a_{f'}}|} + \sum_{1 < a_f < a_{f'} < A_f} \sum_{f=1}^F \frac{Z_{a_f} Z_{a_{f'}} e^2}{|\vec{R}_{a_f} - \vec{R}_{a_{f'}}|} \quad (1.1)
 \end{aligned}$$

where it is understood that each nuclear coordinate \vec{R}_{a_f} may ultimately be expressed in terms of \vec{R}_f , Ω_f , and the set $\{\vec{\tau}_f\}$. The sums have been written so as to envision summing first over fragments and then over the nuclei within a given fragment. The electronic eigenvalue problem

$${}^H \Psi(\vec{R}_f, \Omega_f, \{\vec{\tau}_f\}; x_1, \dots, x_N) = E(\vec{R}_f, \Omega_f, \{\vec{\tau}_f\}) \Psi(\vec{R}_f, \Omega_f, \{\vec{\tau}_f\}; x_1, \dots, x_N) \quad \dots \quad (1.2)$$

is then solved for various choices of the center of mass and Euler angles for all fragments. Of course the energy will also depend upon the internal coordinate sets. We indicate this by writing

$$E(\vec{R}_1, \Omega_1, \dots, \vec{R}_F, \Omega_F; \{\vec{\tau}_1\}, \{\vec{\tau}_2\}, \dots, \{\vec{\tau}_F\})$$

More specifically our interest is limited to the electronic ground state energy of the system and so E should be understood as the lowest energy eigenvalue of the electronic hamiltonian. Then subtracting the energies of the isolated fragments - which surely depend only upon the internal coordinates of each fragment - we arrive at a formal expression for the potential energy of interaction and thus the potential energy

surface given by

$$V(\vec{R}_f, \Omega_f; \{\vec{\tau}_f\}) = E(\vec{R}_f, \Omega_f; \{\vec{\tau}_f\}) - \sum_{f=1}^F E(\{\vec{\tau}_f\})$$

The notation suggests that the potential energy surface is to be considered a function of only the external coordinates - the center of mass and the Euler angles - of each of the molecular fragments. Indeed, the internal coordinates parametrize this potential energy surface but they are not varied from point to point. As a matter of fact, however, the potential energy of interaction cannot depend upon the center of mass of the entire system or its orientation in space. Indeed, then, of the $6F$ variables appearing explicitly in the argument of V , we anticipate that six are ignorable with the potential energy actually a function of $6F-6$ variables. We should note that there are special cases, such as the fragments being atoms or linear molecules where the number of ignorable coordinates must be determined individually.

The focus of this thesis is just on two interacting molecules which, with $F = 2$, we designate A and B. To be specific, we might consider two interacting water molecules in which the bond lengths and the bond angles of each water molecules are fixed. Then there are a total of $F = 2$ fragments with $A_1 = 3$ and $A_2 = 3$. There are 18 nuclear coordinates in all, but with each molecule having three internal (fixed) coordinates, there remain twelve external coordinates, the center of mass and three Euler angles for each of the two molecules. Finally, however, six of these 12 coordinates are ignorable, leaving just six coordinates to be varied as we calculate the potential energy surface of two interacting water molecules.

It is then the total electronic ground state energy for various configurations of these molecules which occupies our attention. Rather than solving the Schrödinger eigenvalue problem by the traditional methods - using approximate schemes such as the Hartree-Fock or configuration mixing techniques - we shall use Density Functional Theory. The formal approach of Density Functional Theory is elegant, although it is based upon a very simple idea.

The essential idea is that there exists a functional of the electron density whose value is never less than the exact ground state electronic eigenvalue, and in fact assumes this eigenvalue for the true electronic density. Thus by trying various densities one seeks to minimize this functional, knowing that the minimum value will in fact be the sought-for ground state electronic energy. We discuss this later on in the following chapters. The practical problem however is that explicit expressions for the functional of the density to be used in the calculation are not known. We will obtain an approximate expression for the case that the two molecules are very far apart. Thus our results are applicable in the theory of long-range intermolecular forces.

Having seen how the electron density plays a central role in Density Functional Theory, we therefore see the emergence of research papers in recent years covering the alternative formulation of quantum mechanics of many-electron systems in terms of the electron density rather than the wavefunction.¹ The single-particle density, the total particle electron density in three-dimensional space, is a quantity that can be measured directly by experimental methods like diffraction and scattering.

Now there has been in existence for quite some time a statistical theory which tries to develop a method for the direct evaluation of the electron density bypassing the wave function method, known as the Thomas-Fermi theory.^{2,3} In fact the model proposed by Thomas and Fermi was the first among Density Functional Theories. The essence of the model is that one can give a self-consistent description of motion of the electrons in a potential produced by the nuclei and the electron charge density itself by finding a simultaneous solution to Poisson's equation

$$\nabla^2 \Phi(\vec{r}) = -4\pi\rho(\vec{r}) \quad (1.3)$$

with $\vec{r} \neq 0$

and the electron density below the Fermi surface given by

$$\rho(\vec{r}) = \frac{\{2m[E_f - e\Phi(\vec{r})]\}^{\frac{3}{2}}}{3\pi^2\hbar^3} \quad (1.4)$$

The motivation for writing this latter expression is the electron gas model in which the local kinetic energy per particle is given in terms of the local density :

$$\frac{E_{kin}}{N} = \frac{3}{5} \left\{ \frac{\hbar^2 k_f^2}{2m} \right\} \quad (1.5)$$

with

$$k_f = \left[\frac{3}{8\pi} \rho \right]^{\frac{1}{3}} \quad (1.6)$$

from whence (1.4) is derived.

An alternative derivation of this density is by considering the Energy Functional of the Thomas-Fermi theory which, in its simplest version, has the form

$$E^{TF}[\rho] = \gamma \int \rho(\vec{r})^{\frac{5}{3}} d\vec{r} + \int \rho(\vec{r}) V(\vec{r}) d\vec{r} + \frac{1}{2} e^2 \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + U \quad \dots \quad (1.7)$$

and then performing the variational procedure $\delta E[\rho] = 0$ subject to the constraint

$$\int \rho(\vec{r}) d\vec{r} = N \quad (1.8)$$

Performing such a variation is guaranteed to produce the same density (1.4). In (1.7) the third term is the Coulombic Self-Energy while the fourth term is the repulsive electrostatic energy given by

$$U = \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} \quad (1.9)$$

$V(\vec{r})$ is the electrostatic potential of k nuclei of charges $Z_1 e, Z_2 e, Z_3 e, \dots, Z_k e$ located at vector positions $\vec{R}_1, \vec{R}_2, \vec{R}_3, \dots, \vec{R}_k$:

$$V(\vec{r}) = \sum_{f=1}^F \sum_{a_f=1}^{A_{f1}} \frac{Z_{a_f} e^2}{|\vec{r} - \vec{R}_{a_f}|} \quad (1.10)$$

and γ is a constant: $\gamma = (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2}{2m}$. $V(\vec{r})$ is connected with $\Phi(\vec{r})$ by

$$e\Phi(\vec{r}) = V(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}') e^2}{|\vec{r} - \vec{r}'|} \quad (1.11)$$

In the Thomas-Fermi-Dirac model,⁴ Dirac considered including an "exchange energy" contribution based from the electron gas expression, so that the Energy Functional takes the form

$$E^{\text{TFD}}[\rho] = E^{\text{TF}}[\rho] - C_e \int \rho(\vec{r})^{\frac{4}{3}} d\vec{r} \quad (1.12)$$

where C_e is a positive constant. The variational procedure is again applied to obtain the density. But for this case, the variation

$$\delta \left[E[\rho] - \mu \left\{ \int d\vec{r} \rho(\vec{r}) - N \right\} \right] = 0 \quad (1.13)$$

will yield a density of the form

$$\rho(\vec{r}) = \left\{ \frac{3}{10\gamma} \left[\frac{20}{3} \gamma e \{ \Phi(\vec{r}) - \Phi_0 \} + \frac{16}{9} C_e^2 \right]^{\frac{1}{2}} + \frac{2 C_e}{5\gamma} \right\}^3 \quad (1.14)$$

But both of these models still neglects two effects that can be important in many-body systems: the correlation between particles and the variations that might exist in the potential. It is clear from (1.4) that the approximation fails when $V(\vec{r})$ becomes infinitely negative near a nucleus since ρ must be infinite if we solve Schrödinger's equations. The models also suffer from the absence of molecular binding - a consequence of the "no-binding" theorem discovered by E. Teller,⁵ whose proof was brought into full rigour by Balazs.⁶ The theorem shows that if the density $\rho(\vec{r})$ is expressed as a local function of the electric potential alone, then there will be no molecular binding. In the Thomas-Fermi and Thomas-Fermi-Dirac theory, the density is related to $\Phi(\vec{r})$ algebraically as in (1.4) and (1.14). Whenever $\rho = f(\Phi)$, no stable

molecule can be formed: The nuclei seek infinite separation from one another. Binding can only occur if there exists a range of internuclear separations for which the forces on the nuclei are attractive.

Nevertheless, binding is displayed in the von-Weizsacker correction. The Thomas-Fermi-von-Weizsacker⁷ Energy Functional has the form

$$E^{\text{TFW}}[\rho] = E^{\text{TF}}[\rho] + \delta \int \{V[\rho(\vec{r})]^{\frac{1}{2}}\}^2 \quad (1.15)$$

where δ is a constant. The variational procedure is again applied to obtain the optimum density $\rho(\vec{r})$. The variation implies that $\rho(\vec{r})$ satisfies

$$\begin{aligned} \frac{5}{3} \gamma \rho^{\frac{2}{3}}(\vec{r}) - 4 \delta \frac{\nabla^2 \rho^{\frac{1}{2}}(\vec{r})}{\rho^{\frac{1}{2}}(\vec{r})} - e V(\vec{r}) + \\ e^2 \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} - \frac{4}{3} C_e \rho^{\frac{1}{3}}(\vec{r}) - \mu = 0 \end{aligned} \quad (1.16)$$

We see that due to the presence of the derivative of the density in the second term in this equation, the density is not directly connected to the potential in an algebraic manner, and from Teller's theorem this indicates that there might exist molecular binding.

The most complicated and least analyzed of all the Thomas-Fermi models is the one that involves the combination of all three:⁸

$$E^{\text{TFDW}}[\rho] = E^{\text{TF}}[\rho] - C_e \int \rho(\vec{r})^{\frac{4}{3}} d\vec{r} + \delta \int \{V[\rho(\vec{r})]^{\frac{1}{2}}\}^2 d\vec{r} \dots \quad (1.17)$$

But for the present context we shall not dwell too much on the Thomas-Fermi model and its subsequent developments and modifications,

but rather we confine ourselves to the modern developments of Density Functional Theory, particularly beginning from the remarkable theorem due to Pierre Hohenberg and Walter Kohn.⁹ This theorem states that for both degenerate and non-degenerate ground states of many-electron systems, there exists an Energy Functional of the density which is an upper bound to the ground state energy for all densities and equals the exact ground state energy for the exact density. This means that all information about the ground state of molecules can be obtained once we obtain the density function. We shall look more closely at the Hohenberg-Kohn theorem and its proofs in the next chapter.

In 1972, R. Gordon and Y.S. Kim proposed a model¹⁰ which describes inter-molecular potential energy of interaction between closed-shell systems using the electron density $\rho(\vec{r})$. In obtaining the energy, the Gordon-Kim model is based upon three approximations :-

- (i) When the atoms approach one another, there are no rearrangement or distortion of the atomic densities; the total density is the superposition of individual atomic densities: $\rho(\vec{r}) = \rho_A(\vec{r}) + \rho_B(\vec{r})$.
- (ii) The Coulombic interaction between all charges are calculated by using additive electron densities. The kinetic, exchange and correlation energy of the electrons are evaluated using the uniform electron-gas approximation.
- (iii) In constructing $\rho(\vec{r})$, atomic Hartree-Fock wave-functions are used.

Within the context of determining the ground-state electronic properties of a large number of different types of interacting closed shell systems, the Gordon-Kim model is very successful. The same authors used the model to evaluate the interactions of rare-gas atoms and halide crystals.¹¹

Nevertheless, the theory describes accurately only the potentials between closed shell systems at shorter distances out to the potential minima. It fails to give accurate descriptions of the entire potential curve. According to Harris,¹² the model has flaws in that it is quite unclear how the full form of the induction and dispersion forces are incorporated within the scheme of the theory; only lowest order induction effects are included, since the densities are additive in the undistorted molecular densities.

Using mean field electron densities, Harris managed to remove a part of the flaw of the theory - the inclusion of induction forces. However, he only partially solved the dispersion-forces problem. It is our intent to display in our work both the induction and dispersion terms for the case of two molecules interacting via long-range interactions within the context of Density Functional Theory.

The understanding of the properties of dispersive forces is vital in forecasting some practical consequences of the way molecules behave: for example, the additivity of the dispersive forces represents the fact of general cohesion.¹³ In this thesis, we show as a preliminary calculation the origin of the term "dispersion" as first coined by London in 1932; that we obtain a term in the second order energy correction to the system of two molecules as a dispersion integral.

In 1980, the formalism of Density Functional Theory received yet another boost when Mel Levy and Karl Freed¹⁴ developed an algorithm for determining the Energy Functional. Using an external "driving potential" term, they managed to obtain a Taylor expansion for the "exact" Energy Functional about a reference density. This formulation is a generalization of the Hohenberg-Kohn theorem in that it takes advantage of

an arbitrary choice of expansion point. We shall look more closely into Fred and Levy's formulation in the next chapter.

So powerful is the idea purported by Density Functional Theory in that the three-dimensional particle density $\rho(\vec{r})$ should be a fundamental carrier of physical information about a system and thus bypassing the wave-function that the formalism has been extended, with success, to spin-polarised systems,¹⁵ relativistic systems,^{16,17} and also to any excited states that correspond to the lowest state of a given symmetry (see reference 18). There are also suggestions to extend the formalism completely to a dynamical Density Functional Theory and therefore considering extending the Hohenberg-Kohn theorem to include a time-dependent oscillating potential.^{19,20}

CHAPTER II

DENSITY FUNCTIONAL THEORY

The modern formalism of Density Functional Theory rests on the powerful theorem by Hohenberg and Kohn that states that there exists an Energy Functional of the density which is an upper bound to the ground-state energy. If this Energy Functional is minimized with respect to the density, i.e. finding $E[\rho]$

$$\frac{\delta E[\rho]}{\delta \rho} = 0 \quad \text{subject to} \quad \int d\vec{r} \rho(\vec{r}) = N \quad (2.1)$$

an Euler equation will be yielded which can be a deterministic equation for $\rho(\vec{r})$. However, since no one can write down the actual form of the Energy Functional, we have to invoke some approximations. In this chapter, we will review the theorem due to Hohenberg and Kohn and then move to one way of approximating the Energy Functional using Taylor's expansion as firstly suggested by Freed and Levy.

In demonstrating the Hohenberg-Kohn theorem, let us use the language of second quantization: we define $\psi^\dagger(x)$ and $\psi(x)$ as local field creation and annihilation operators. If we now consider a very large box containing an arbitrary number of electrons moving under the influence of an external potential $v(\vec{r})$, the Hamiltonian of the system is given by

$$H = T + V + U \quad (2.2)$$

where
$$T = \frac{\hbar^2}{2m} \int \nabla \psi^\dagger(\mathbf{x}) \cdot \nabla \psi(\mathbf{x}) d\mathbf{x} \quad (2.3)$$

$$V = \int v(\mathbf{x}) \psi^\dagger(\mathbf{x}) \psi(\mathbf{x}) d\mathbf{x} \quad (2.4)$$

$$U = \frac{1}{2} \iint \frac{1}{|\vec{r} - \vec{r}'|} \psi^*(\mathbf{r}) \psi^*(\mathbf{r}') \psi(\mathbf{r}) \psi(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (2.5)$$

We stress that we deal, for simplicity, only with situations in which the ground state is nondegenerate. The electron density is defined as

$$\rho(\vec{r}) = \langle \Psi | \sum_{\xi} \psi^\dagger(\vec{r}, \xi) \psi(\vec{r}, \xi) | \Psi \rangle. \quad (2.6)$$

$\rho(\vec{r})$ is thus a functional of $v(\vec{r})$ since clearly v determines the ground state $|\Psi\rangle$.

Theorem

The converse of this statement is also true: $v(\vec{r})$ is a functional uniquely determined by $\rho(\vec{r})$.

Proof

Let us assume there exists another potential $v'(\vec{r})$ with ground state Ψ' that produces the same density $\rho(\vec{r})$. Now Ψ' cannot be equal to Ψ since they are eigenvectors of different Schrodinger equations. Thus if H and H' are the Hamiltonians associated with Ψ and Ψ' and generate ground state energies \mathcal{E} and \mathcal{E}' :

$$H |\Psi\rangle = \mathcal{E} |\Psi\rangle \quad \text{and} \quad H' |\Psi'\rangle = \mathcal{E}' |\Psi'\rangle$$

where $H = H^0 + V$ and $H' = H^0 + V'$, then due to the minimal property of the ground state,

$$E' = \langle \Psi' | H' | \Psi' \rangle \quad (2.7)$$

$$< \langle \Psi | H' | \Psi \rangle$$

where $\langle \Psi | H' | \Psi \rangle = \langle \Psi | H + V' - V | \Psi \rangle$

$$= \langle \Psi | H_0 + V + V' - V | \Psi \rangle \quad (2.8)$$

Therefore $E' < E + \int [\bar{u}'(\vec{r}) - u(\vec{r})] \rho(\vec{r}) d\vec{r}$ (2.9)

If we interchange the primed and unprimed quantities and go through the same procedure, we find that

$$E < E' + \int [\bar{u}(\vec{r}) - u'(\vec{r})] \rho(\vec{r}) d\vec{r} \quad (2.10)$$

Adding together, we are led to the inconsistent result that

$$E + E' < E + E' \quad (2.11)$$

Clearly, our assumption concerning u' leading to the same density ρ cannot be correct. Therefore within a constant, we have shown that $u(\vec{r})$ is uniquely determined by the density $\rho(\vec{r})$ and so due to $u(\vec{r})$ fixing a particular Hamiltonian in (2.4) and (2.2), we see that the full many-particle ground state is also uniquely determined by the density $\rho(\vec{r})$, completing the proof of the theorem.

Another aspect of the Hohenberg-Kohn theorem concerns itself with the Energy Functional defined by

$$E_{\text{v}}[\rho'(\vec{r})] \equiv \int v(\vec{r})\rho'(\vec{r})d\vec{r} + F[\rho'(\vec{r})] \quad (2.12)$$

where $F[\rho'(\vec{r})] \equiv \langle \Psi' | T + V | \Psi' \rangle \quad (2.13)$

is a universal functional of a "v-representable" density and Ψ' being the ground state eigenfunction uniquely determined by ρ' according to the previous theorem. By "v-representability" we mean the trial density is required to be the ground state density associated with some local external potential.

Theorem

$E_{\text{v}}[\rho']$ assumes its minimum value for the true ground state density $\rho(\vec{r})$ under the restriction

$$N[\rho] = \int \rho(\vec{r})d\vec{r} = N \quad (2.14)$$

Proof

The quantum mechanical variational principle states that for a system of N particles, the Energy Functional of Ψ' , $E_{\text{v}}[\Psi']$ which is written as

$$E_{\text{v}}[\Psi'] \equiv V \langle \Psi' | V | \Psi' \rangle + \langle \Psi' | T + U | \Psi' \rangle \quad (2.15)$$

$$\geq E_{\text{v}}[\Psi]$$

has a minimum at the correct ground state wavefunction Ψ , relative to variations of Ψ' , in which the number of particles is constant. Let Ψ' be associated with an external potential $u'(\vec{r})$ (different from $u(\vec{r})$). Thus

$$E_u[\rho'(\vec{r})] = \int u(\vec{r})\rho'(\vec{r})d\vec{r} + F[\rho'(\vec{r})] \quad (2.16)$$

where, as the density ρ' implies the wave function Ψ' , then the Energy Functional $E_u[\rho']$ implies the Energy Functional of the density $\mathcal{E}_u[\Psi']$.

Now due to the Rayleigh-Ritz principle, the Energy Functional of the arbitrary wave function Ψ' is bigger than the Energy Functional of the ground state wave function Ψ . Therefore since

$$\mathcal{E}_u[\Psi'] > \mathcal{E}_u[\Psi]$$

this implies that

$$E_u[\rho'(\vec{r})] > E_u[\rho(\vec{r})]$$

where

$$E_u[\rho(\vec{r})] = \int u(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho(\vec{r})] \quad (2.17)$$

where $\rho(\vec{r})$ is the ground state density. This establishes the minimal property of $E[\rho'(\vec{r})]$

We now see the thorough simplification brought about by the Hohenberg-Kohn theorem: that the major part of solving many-electron

problems are associated with the determination of $F[\rho]$: if $F[\rho]$ were a known and simple functional of $\rho(\vec{r})$, the determination of the ground-state energy in a given external potential would not be difficult, since the only thing required is the minimization of a functional of a three-dimensional density function.

Since its debut in 1964, many works have been produced to improve and generalize the Hohenberg-Kohn theorem. It was even shown²¹ that the theorem is a special case where the constraints are expressed by the expectation values of an indenumerable set of charge density operator, the members of which are indexed by the continuum of eigenvalues of the single particle position operator. One could also obtain²² the energy as solutions to a first order nonlinear partial differential equation.

What is needed now is an exact and explicit form for the Energy Functional $E[\rho]$. Mel Levy and K. Freed provides an abstract theorem that derives $E[\rho]$ as a Taylor expansion of $\delta\rho(\vec{r})$ where

$$\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0(\vec{r}) \quad (2.18)$$

and $\rho_0(\vec{r})$ is a certain reference density.

In discussing Levy and Freed's formulation, it is important to mention that while Hohenberg and Kohn restricts the functional $F[\rho]$ to be "v-representable", Levy and Freed lifts this restriction. To begin with, the Energy Functional of Levy and Freed is defined as

$$E[\rho] = \min_{\{\Psi\}} \{ \langle \Psi | H | \Psi \rangle_{\rho} \} \quad (2.19)$$

The notation implies minimizing the expectation value by searching through the class of wavefunctions $|\Psi\rangle_\rho$ each of which yields the specified density:

$$\rho(\vec{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle_\rho \quad (2.20)$$

assuming that $|\Psi\rangle_\rho$ is normalized:

$$\langle \Psi | \Psi \rangle_\rho = 1 \quad (2.21)$$

$\hat{\rho}$ is the sum of one-body operators given by

$$\hat{\rho}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i) \quad (2.22)$$

To minimize (2.19), we minimize the auxilliary functional defined by Levy and Freed as

$$\begin{aligned} \mathcal{F}[\rho] = & \{ \langle \Psi | H | \Psi \rangle + \int d\mathbf{r} \lambda(\mathbf{r}) \{ \langle \Psi | \rho | \Psi \rangle - \rho(\mathbf{r}) \} \\ & - \mathcal{E} \{ \langle \Psi | \Psi \rangle - 1 \} \} \end{aligned} \quad (2.23)$$

If the wave function $\langle \Psi |$ or $|\Psi\rangle$ is subjected to a variation, say

$$\langle \Psi | \rightarrow \{ \langle \Psi | + \langle \delta \Psi | \}$$

then we envision obtaining a corresponding variation in the functional

$$\delta \mathcal{F} = \langle \delta \Psi | \{ H + \int d^3r \lambda(\vec{r}) \rho(\vec{r}) - \mathcal{E} \} | \Psi \rangle \quad (2.24)$$

The $\lambda(\vec{r})$ is a Lagrange multiplier function used in the minimization

procedure, for we will have to set $\delta \mathcal{F} = 0$ to obtain the optimum $\rho(\vec{r})$ for the purpose of evaluating the Energy Functional in order to get the ground state energy.

The way to do this is by inverting the form of $\lambda(\vec{r})$ and obtain ρ in terms of λ : This inversion is derived from (2.20) with $|\Psi\rangle$ being a function of λ . From (2.20) one obtains

$$\rho(\vec{r}) = \rho^0(\vec{r}) + \int d\vec{r}' K^{-1}(\vec{r}, \vec{r}') \lambda(\vec{r}') + \mathcal{O}(\lambda^2) \quad (2.25)$$

where $K^{-1}(\vec{r}, \vec{r}')$ is a quantity called the density-density correlation function which will be defined and derived in the forthcoming chapters. If we define the inverse of this correlation function :

$$\int K(\vec{r}, \vec{r}'') K^{-1}(\vec{r}'', \vec{r}') d\vec{r}'' = \delta(\vec{r} - \vec{r}') \quad (2.26)$$

then equation (2.25) can be inverted to give

$$\lambda(\vec{r}) = \int d\vec{r}' K(\vec{r}, \vec{r}') \{\rho(\vec{r}') - \rho^0(\vec{r}')\} + \mathcal{O}(\delta\rho)^2 \quad (2.27)$$

and we can use this expression to write the Energy as a functional of the density.

All of this will be dealt with in more detail in chapters 4 and 5. Before using the Levy and Freed formalism to construct the Energy Functional, we review in the next chapter the traditional theory of long-range intermolecular forces based upon the Rayleigh-Schrodinger Perturbation Theory (RSPT). This formalism will be used again in chapter IV when we include the "driving potential" of Levy and Freed.

CHAPTER III

THE FIRST- AND SECOND-ORDER CORRECTION
TO THE ENERGY OF THE SYSTEM

Our system in consideration consists of two neutral molecules A and B whose ground state eigenfunction do not overlap (i.e. we consider both A and B separated farther than the sum of their van der Waal's radii and therefore disregard any considerations of short-range forces). Molecule A has A nuclei-centers and N_A electrons while molecule B has B nuclei centers and N_B electrons. Since the wavefunctions of the electrons do not overlap within the space of each other as the electrons only act from a distance, the total asymptotic (i.e. infinite separation) ground-state energy of the system is given by

$$E^0 = E_A^0 + E_B^0 \quad (3.1)$$

The problem of determining the interaction energy between these two molecules reduces in principle to obtaining the ground state electronic eigenvalue of a Hamiltonian which can be partitioned into the sum of the Hamiltonians of the isolated molecules $H_A^0 + H_B^0$ plus the Coulombic interactions V between all the charges in molecule A and those in B, i.e.

$$H = H_A^0 + H_B^0 + V \quad (3.2)$$

where

$$H_A^0(1, \dots, N_A) = T_A + V_{ee}^A + V_{en}^A + V_{nn}^A \quad (3.3)$$

$$\text{and} \quad H_B^O(N_A+1, \dots, N_A+N_B) = T_B + V_{ee}^B + V_{en}^B + V_{nn}^B \quad (3.4)$$

where, if written explicitly,

$$V_{ee}^A = \sum_{i < i'} \frac{e^2}{|\vec{r}_i - \vec{r}_{i'}|} \quad (3.5a)$$

$$V_{en} = \sum_i \sum_{\alpha} \frac{-Z_{\alpha} e^2}{|\vec{r}_i - \vec{R}_{\alpha}|} \quad (3.5b)$$

$$V_{nn}^A = \sum_{\alpha < \alpha'} \frac{Z_{\alpha} Z_{\alpha'} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\alpha'}|} \quad (3.5c)$$

$$V_{ee}^B = \sum_{j < j'} \frac{e^2}{|\vec{r}_j - \vec{r}_{j'}|} \quad (3.6a)$$

$$V_{en}^B = \sum_j \sum_{\beta} \frac{-Z_{\beta} e^2}{|\vec{r}_j - \vec{R}_{\beta}|} \quad (3.6b)$$

$$V_{nn}^B = \sum_{\beta < \beta'} \frac{Z_{\beta} Z_{\beta'} e^2}{|\vec{R}_{\beta} - \vec{R}_{\beta'}|} \quad (3.6c)$$

The system of notation we follow is as such: the limits on the sums over i , the electron index in molecule A, are from $i = 1$ to $i = N_A$ and the limits on the sums over the electron index j of molecule B are from $j = N_A+1$ to $N_A + N_B$. Z_{α} and Z_{β} , the nuclei index for molecule A and B respectively, have limits ranging from 1 to A and B respectively. For purposes of simplifying the notations, we will not write these limits explicitly, but for example, \sum_j should always be understood as $\sum_{j=N_A+1}^{N_A+N_B}$.

Now the eigenstate of the Hamiltonian $H_A^0 + H_B^0$ can be written as

$$\Psi \equiv \Psi_A^0(x_1, \dots, x_{N_A}) \Psi_B^0(x_{N_A+1}, \dots, x_{N_A+N_B}) \quad (3.7)$$

where Ψ_A^0 and Ψ_B^0 are the eigenstates of the individual Hamiltonians H_A^0 and H_B^0 and we have ignored antisymmetry. It is also worth noting that while the Hamiltonian H is totally symmetric under the interchange of any pair of the $(N_A + N_B)$ electron labels, neither H_A^0 , H_B^0 nor V in (3.2) is separately symmetric under the interchange of particle labels.

In (3.2), the Coulombic potential V can be written explicitly as

$$V = \sum_j \sum_\alpha \frac{-z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_i \sum_\beta \frac{-z_\beta e^2}{|\vec{r}_i - \vec{R}_\beta|} + \sum_i \sum_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_\alpha \sum_\beta \frac{z_\alpha z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \quad \dots \quad (3.8)$$

The first term denotes the interaction between the electrons in molecule B with the nuclei in molecule A, while the second term denotes the interaction between the electrons in molecule A with the nuclei in molecule B. The next two terms are the electron-electron interaction and the nuclear-nuclear repulsion of A and B.

Now if we regard V to be perturbations to the total Hamiltonian of the system, we can find the first and second order correction to the energy using perturbation theory. Let us recall that in the Rayleigh-Schrödinger Perturbation Theory, (RSPT), the first and second order energy correction are given by the formulae

$$E^{(1)} = \langle \Psi^0 | V | \Psi^0 \rangle \quad (3.9)$$

and

$$E^{(2)} = \sum_{v \neq 0} \frac{|\langle \Psi^v | V | \Psi^0 \rangle|^2}{E^v - E^0} \quad (3.10)$$

respectively, where Ψ^0 is the ground state of the unperturbed Hamiltonian, assumed to be normalised and v is an index that denotes the excited states of the system.

Applying the RSPT to our system in consideration, we can write the first-order energy correction as

$$\begin{aligned} E^{(1)} &= \langle \Psi_{AB}^0 \Psi_{AB}^0 | V | \Psi_{AB}^0 \Psi_{AB}^0 \rangle \\ &= \langle \Psi_{AB}^0 \Psi_{AB}^0 | \sum_j \sum_{\alpha} \frac{-Z_{\alpha} e^2}{|\vec{r}_j - \vec{R}_{\alpha}|} | \Psi_{AB}^0 \Psi_{AB}^0 \rangle + \langle \Psi_{AB}^0 \Psi_{AB}^0 | \sum_i \sum_{\beta} \frac{-Z_{\beta} e^2}{|\vec{r}_i - \vec{R}_{\beta}|} | \Psi_{AB}^0 \Psi_{AB}^0 \rangle \\ &\quad + \langle \Psi_{AB}^0 \Psi_{AB}^0 | \sum_i \sum_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} | \Psi_{AB}^0 \Psi_{AB}^0 \rangle + \langle \Psi_{AB}^0 \Psi_{AB}^0 | \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} | \Psi_{AB}^0 \Psi_{AB}^0 \rangle \\ &\quad \dots \quad (3.11) \end{aligned}$$

The first term can be written out as

$$\begin{aligned} &\int d\vec{x}_1 \dots d\vec{x}_{N_A} d\vec{x}_{N_A+1} \dots d\vec{x}_{N_A+N_B} \Psi_A^{0*}(\vec{x}_1, \dots, \vec{x}_{N_A}) \Psi_B^{0*}(\vec{x}_{N_A+1}, \dots, \vec{x}_{N_A+N_B}) \\ &\times \sum_{\alpha} \sum_j \frac{-Z_{\alpha} e^2}{|\vec{r}_j - \vec{R}_{\alpha}|} \Psi_A^0(\vec{x}_1, \dots, \vec{x}_{N_A}) \Psi_B^0(\vec{x}_{N_A+1}, \dots, \vec{x}_{N_A+N_B}) \quad (3.12) \end{aligned}$$

The electron coordinates in the molecule A wave function can be integrated due to the fact that the interaction is only between the nuclei in A and the electrons in B. Therefore the molecule A wave-function can be collected together and integrated to give

$$\int dx_1 \dots dx_{N_A} \Psi_A^0(x_1, \dots, x_{N_A}) \Psi_A^0(x_1, \dots, x_{N_A}) = 1 \quad (3.13)$$

since it is assumed to be normalised. We are now left with evaluating

$$\begin{aligned} & \int dx_{N_A+1} \dots dx_{N_A+N_B} \Psi_B^{0*}(x_{N_A+1}, \dots, x_{N_A+N_B}) \Psi_B^0(x_{N_A+1}, \dots, x_{N_A+N_B}) \\ & \times \sum_{\alpha} \sum_j \frac{-Z_{\alpha} e^2}{|\vec{r}_j - \vec{R}_{\alpha}|} \end{aligned} \quad (3.14)$$

Now for the purpose of simplifying the equations, let I denote any one of the coordinates in set A and J be any one of the coordinates in set B. Specifically for the present purpose let $I \equiv 1$ and $J \equiv N_A + 1$. Then for example the probability density of the B molecule is written as

$$P_B(x_J) = \int dx_{N_A+2} \dots dx_{N_A+N_B} \Psi_B^{0*} \Psi_B^0 \quad (3.15)$$

so that (3.14) becomes $\left[(N_A + N_B) - N_A \right] \sum_{\alpha} \int dx_J P_B(x_J) \frac{-Z_{\alpha} e^2}{|\vec{r}_J - \vec{R}_{\alpha}|}$

$$\text{Let} \quad \int dx_J \equiv \sum_{\xi_J} \int d^3 r_J \quad (3.16)$$

where we have indicated a summation over spin states and an integration over ordinary three-dimensional space. Thus our term becomes

$$\sum_{\alpha} N_B \sum_{\xi_J} \int d^3 r_J \frac{P_B(\vec{r}_J, \xi_J) - Z_{\alpha} e^2}{|\vec{r}_J - \vec{R}_{\alpha}|} \quad (3.17)$$

But according to definition, $N_B \sum_{\xi_J} P_B(\vec{r}_J, \xi_J)$ is just the electron density of molecule B, written as

$$\begin{aligned} \rho_B(\vec{r}_J) &\equiv N_B \sum_{\xi_J} P_B(\vec{r}_J, \xi_J) \\ &\equiv \langle \Psi_B^0 | \sum_j \delta(\vec{r}_J - \vec{r}_j) | \Psi_B^0 \rangle \end{aligned} \quad (3.18)$$

Thus our expression for the first term becomes

$$-e^2 \sum_{\alpha} Z_{\alpha} \int d^3 r_J \frac{\rho_B(\vec{r}_J)}{|\vec{r}_J - \vec{R}_{\alpha}|} \quad (3.19)$$

Likewise, the other three terms in (3.11) can be simplified in terms of these density functions and we write the first order correction to the energy (after all integrations are performed) as

$$\begin{aligned} E^{(1)} &= -e^2 \sum_{\alpha} Z_{\alpha} \int d^3 r_J \frac{\rho_B(\vec{r}_J)}{|\vec{r}_J - \vec{R}_{\alpha}|} - e^2 \sum_{\beta} Z_{\beta} \int d^3 r_I \frac{\rho_A(\vec{r}_I)}{|\vec{r}_I - \vec{R}_{\beta}|} \\ &+ e^2 \iint d^3 r_I d^3 r_J \frac{\rho_A(\vec{r}_I) \rho_B(\vec{r}_J)}{|\vec{r}_I - \vec{r}_J|} + \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} \end{aligned} \quad (3.20)$$

where for example $\rho_A(\vec{r}_I) = N_A \sum_{\xi_I} P_A(\vec{r}_I, \xi_I) = N_A \sum_{\xi_I} \int \prod_{i \neq I} dx_i \Psi_A^{0*} \Psi_A^0$

This expression that we obtained is just the lowest order electrostatic contribution to the intermolecular potential energy, using wavefunctions without polarization. We proceed next to observe the form of the second order correction to the energy of the system. From second order Perturbation theory,

$$E^{(2)} = \sum_{\substack{\lambda, \kappa \\ \neq 0}} \frac{|\langle \psi_A^0 \psi_B^0 | V | \psi_A^\lambda \psi_B^\kappa \rangle|^2}{E_A^0 + E_B^0 - E_A^\lambda - E_B^\kappa} \quad (3.21)$$

where V is our four-term Coulombic perturbation. At this point let us mention that the wave function $|\psi_A^0 \psi_B^0\rangle$ can be written as a direct product since we ignore antisymmetry :

$$|\psi_A^0 \psi_B^0\rangle \equiv |\psi_A^0\rangle |\psi_B^0\rangle \quad (3.22)$$

Similar is the case for the excited states $|\psi_A^\lambda \psi_B^\kappa\rangle$ if we are to ignore antisymmetry. The direct product basis $\{|\psi_A^\lambda\rangle |\psi_B^\kappa\rangle\}$ forms an orthonormal set, a fact which can be seen if we consider the eigenvalue equations

$$H_A^0 |\psi_A^\lambda\rangle = E_A^\lambda |\psi_A^\lambda\rangle \quad (3.23)$$

$$H_B^0 |\psi_B^\kappa\rangle = E_B^\kappa |\psi_B^\kappa\rangle \quad (3.24)$$

From whence

$$\langle \psi_A^\lambda | \psi_A^{\lambda'} \rangle = \delta_{\lambda\lambda'} \quad (3.25)$$

$$\langle \psi_B^\kappa | \psi_B^{\kappa'} \rangle = \delta_{\kappa\kappa'} \quad (3.26)$$

so that

$$\begin{aligned}
 \langle \Psi_{AB}^{\lambda\kappa} | \Psi_{AB}^{\lambda'\kappa'} \rangle &= \langle \Psi_A^{\lambda} | \langle \Psi_B^{\kappa} | | \Psi_A^{\lambda'} \rangle | \Psi_B^{\kappa'} \rangle \\
 &= \delta_{\lambda\lambda'} \delta_{\kappa\kappa'}
 \end{aligned} \tag{3.27}$$

In (3.21) the expression involves sums over the excited zeroth order states of the molecules. We often speak of "virtual excitations" of the molecules to describe the terms in the expansion. So in effect we have a combination of three possibilities: one when molecule A only is "virtually excited" and molecule B stays in the ground state condition, another when molecule B is "virtually excited" and A stays in the ground state condition, and the third condition wherein both molecules are "virtually" excited. Therefore we have

$$\begin{aligned}
 E^{(2)} = & \sum_{\lambda \neq 0} \frac{|\langle \Psi_{AB}^{\lambda\psi^0} | V | \Psi_{AB}^{\psi^0\psi^0} \rangle|^2}{(E_A^{\lambda} - E_A^{\psi^0})} + \sum_{\kappa \neq 0} \frac{|\langle \Psi_{AB}^{\psi^0\kappa} | V | \Psi_{AB}^{\psi^0\psi^0} \rangle|^2}{(E_B^{\kappa} - E_B^{\psi^0})} + \sum_{\substack{\lambda, \kappa \\ \neq 0}} \frac{|\langle \Psi_{AB}^{\lambda\kappa} | V | \Psi_{AB}^{\psi^0\psi^0} \rangle|^2}{(E_A^{\psi^0} + E_B^{\psi^0}) - (E_A^{\lambda} + E_B^{\kappa})} \\
 & \dots
 \end{aligned} \tag{3.28}$$

Let us evaluate the matrix elements and introduce a quantity $\rho^{0\kappa, \lambda}$ and ρ^{00} as well as a transition density function:

$$\begin{aligned}
 \rho^{0\kappa}(\vec{r}_J) &\equiv \sum_{\xi_J} \int \prod_{j \neq J} dx_j \Psi_B^{0*} \Psi_B^{\kappa} \\
 \rho_B^{0\kappa} &\equiv N_B \rho_B^{0\kappa}(\vec{r}_J)
 \end{aligned} \tag{3.29}$$

Using the fact that the N_A indices $i = 1, \dots, N_A$ are all equivalent and the N_B indices are also equivalent ($j = N_A + 1, \dots, N_A + N_B$) we arrive at the following expression for the second order energy correction:-

$$\begin{aligned}
E^{(2)} = & \sum_{\kappa} \left| \iint d^3r_I d^3r_J \rho_A^{00}(\vec{r}_I) \rho_B^{0\kappa}(\vec{r}_J) \mathcal{V}(\vec{r}_I, \vec{r}_J) \right|^2 + \\
& \sum_{\lambda} \left| \iint d^3r_I d^3r_J \rho_A^{0\lambda}(\vec{r}_I) \rho_B^{00}(\vec{r}_J) \mathcal{V}(\vec{r}_I, \vec{r}_J) \right|^2 + \\
& \sum_{\lambda} \sum_{\kappa} \left| \iint d^3r_I d^3r_J \rho_A^{0\lambda}(\vec{r}_I) \rho_B^{0\kappa}(\vec{r}_J) \mathcal{V}(\vec{r}_I, \vec{r}_J) \right|^2 \quad (3.30)
\end{aligned}$$

where I is the prototype for the electrons in molecule A and J the prototype for the electrons in molecule B. The $\mathcal{V}(\vec{r}_I, \vec{r}_J)$ is defined as

$$\begin{aligned}
\mathcal{V}(\vec{r}_I, \vec{r}_J) = & N_A \sum_{\beta} \frac{-Z_{\beta} e^2}{|\vec{r}_I - \vec{R}_{\beta}|} + N_B \sum_{\alpha} \frac{-Z_{\alpha} e^2}{|\vec{r}_J - \vec{R}_{\alpha}|} + \frac{N_A N_B e^2}{|\vec{r}_I - \vec{r}_J|} + \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} \\
& \dots \quad (3.31)
\end{aligned}$$

Our expression for the second order correction to the energy can be written in terms of multipole-moment expansions. But before doing so let us observe the orientation of the two molecules in space and note that they can be looked upon as being in a common coordinate system even though each molecule has got different coordinate systems distinct from each other.

From figure 1 we can deduce the transformation from a global coordinate system where all nuclei and electrons of the "supermolecule" have a common axis to a pair of local coordinate systems each located within the respective molecule (say at the center of mass):

$$\begin{aligned}
\vec{r}_I &= \vec{D}_A + \vec{\zeta}_I & ; & & \vec{r}_J &= \vec{D}_B + \vec{\zeta}_J \\
\vec{R}_{\alpha} &= \vec{D}_A + \vec{\zeta}_{\alpha} & ; & & \vec{R}_{\beta} &= \vec{D}_B + \vec{\zeta}_{\beta} \quad (3.32)
\end{aligned}$$

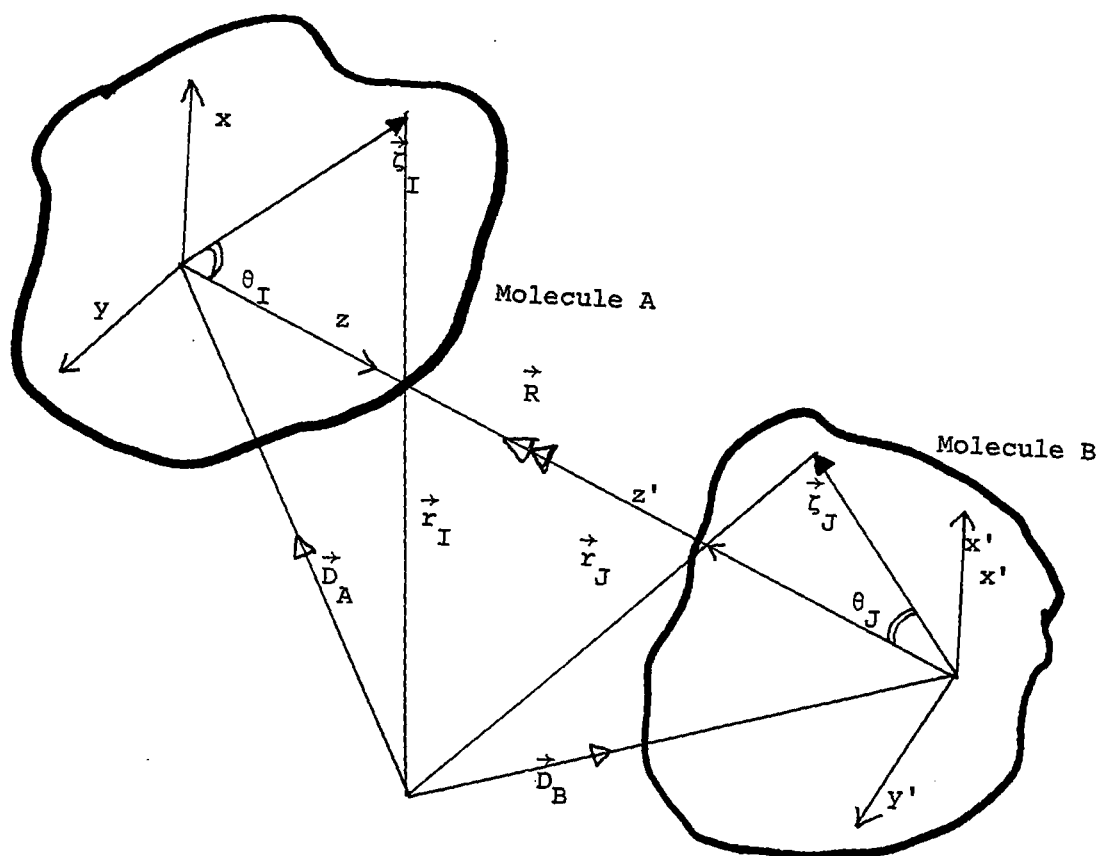


Figure 1: Relative Orientation of the Two Molecules in a New Coordinate System

Thus it follows that

$$\begin{aligned}
 \vec{r}_J - \vec{R}_\alpha &= -\vec{R} + \vec{\zeta}_J - \vec{\zeta}_\alpha \\
 \vec{r}_I - \vec{R}_\beta &= \vec{R} + \vec{\zeta}_I - \vec{\zeta}_\beta \\
 \vec{r}_I - \vec{r}_J &= \vec{R} + \vec{\zeta}_\alpha + \vec{\zeta}_J \\
 \vec{R}_\alpha - \vec{R}_\beta &= \vec{R} + \vec{\zeta}_\alpha - \vec{\zeta}_\beta
 \end{aligned} \tag{3.33}$$

where we have written $\vec{R} = \vec{D}_A - \vec{D}_B$. A more illustrative and practical example is shown in figure 2 where we have shown this coordinate transformation pictorially for the system of two water molecules.

Now let us evaluate the matrix elements of $\mathcal{V}(\vec{r}_I, \vec{r}_J)$ sandwiched between the wave functions $\psi_A^0 \psi_B^0$ using the "two-center expansion" for a charge distribution.^{23,24} For example, we can write

$$\begin{aligned}
 \frac{1}{|\vec{R}_\alpha - \vec{R}_\beta|} &= \frac{1}{|\vec{R} + \vec{\zeta}_\alpha - \vec{\zeta}_\beta|} \\
 &= \sum_{n_a, n_b=0}^{\infty} \sum_{m=-n_<}^{+n_<} B_{n_a, n_b}^{(|m|)}(\zeta_\alpha, \zeta_\beta, R) P_{n_a}^m(\cos \theta_\alpha) P_{n_b}^m(\cos \theta_\beta) \\
 &\quad \times \exp \{im(\phi_\beta - \phi_\alpha)\}
 \end{aligned} \tag{3.34}$$

where the symbols $n_<$ denotes the smaller of n_a and n_b and where the coefficients $B_{n_a, n_b}^{(|m|)}(\zeta_\alpha, \zeta_\beta, R)$ are in general complicated functions of ζ_α and ζ_β . According to Hirschfelder²⁴

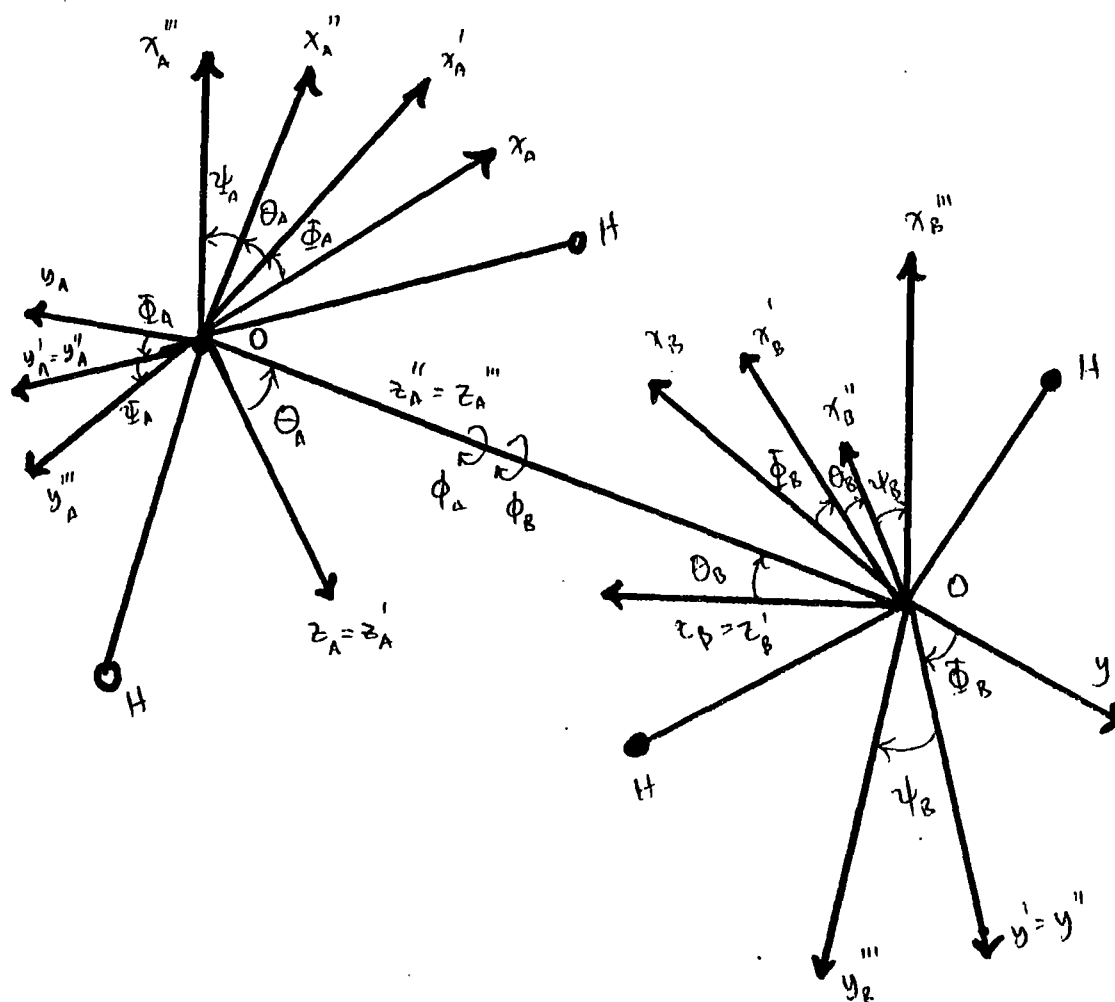


Figure 2: Orientation of Two Water Molecules in a Common Coordinate System

$$B_{n_a, n_b}^{(m)}(\zeta_\alpha, \zeta_\beta; R) = \frac{(-1)^{n_b+m} (n_a + n_b)! \zeta_\alpha^{n_a} \zeta_\beta^{n_b}}{(n_a + |m|)! (n_b + |m|)! R^{n_a + n_b + 1}} \quad (3.35)$$

provided that $R > (\zeta_\alpha + \zeta_\beta)$, i.e., the two charge distributions do not overlap, which is the case in question. Note that throughout we have used Roman or Greek letters without the arrow to indicate their corresponding vector magnitude, i.e.

$$\zeta_\alpha \equiv |\vec{\zeta}_\alpha| \quad \text{etc.}$$

The angles θ_A and θ_B are defined with respect to the centers a and b as shown in figure 1. Note that we have defined the z-axis to be orientated along the line joining the centers of the coordinate systems of the two molecules. Substituting some values for n_a and n_b as well as m, we get for the first few multipole-multipole interactions,

$$\text{monopole-monopole ;-- } n_a = 0, n_b = 0, m = 0 \quad (3.36)$$

$$\begin{aligned} \text{monopole-dipole :- } n_a = 0, n_b = 1, m = 0 \\ n_a = 1, n_b = 0, m = 0 \end{aligned} \quad (3.37)$$

$$\begin{aligned} \text{dipole-dipole :- } n_a = 1, n_b = 1, m = -1 \\ n_a = 1, n_b = 1, m = 0 \\ n_a = 1, n_b = 1, m = +1 \end{aligned} \quad (3.38)$$

Therefore our expression for the potential energy operator in terms of the first three multipole interactions is :-

$$\begin{aligned}
\mathcal{V}(\vec{r}_I, \vec{r}_J) &= N_B \sum_{\alpha} -Z_{\alpha} e^2 \left[\frac{1}{R} - \zeta_{\alpha} \frac{\cos \theta_{\alpha}}{R^2} - \frac{2}{R^3} \zeta_{\alpha} \zeta_J \cos \theta_{\alpha} \cos \theta_J \right. \\
&\quad \left. + \frac{1}{R^3} \zeta_J \zeta_{\alpha} \sin \theta_J \sin \theta_{\alpha} \cos(\phi_{\alpha} - \phi_J) \right] \\
&\quad + \\
&\quad N_A \sum_{\beta} -Z_{\beta} e^2 \left[\frac{1}{R} - \zeta_{\beta} \frac{\cos \theta_{\beta}}{R^2} - \zeta_I \frac{\cos \theta_I}{R^2} - 2 \zeta_{\beta} \zeta_I \frac{\cos \theta_{\beta} \cos \theta_I}{R^3} \right. \\
&\quad \left. + \frac{1}{R^3} \zeta_I \zeta_{\beta} \sin \theta_I \sin \theta_{\beta} \cos(\phi_{\beta} - \phi_I) \right] \\
&\quad + N_A N_B e^2 \left[\frac{1}{R} - \frac{1}{R^2} \{ \zeta_J \cos \theta_J + \zeta_I \cos \theta_I \} - \frac{2}{R^3} \zeta_I \zeta_J \cos \theta_I \cos \theta_J \right. \\
&\quad \left. + \zeta_I \zeta_J \sin \theta_I \sin \theta_J \cos(\phi_J - \phi_I) \right] \\
&\quad + \\
&\quad + \sum_{\alpha} \sum_{\beta} Z_{\alpha} Z_{\beta} e^2 \left(\frac{1}{R} - \frac{\zeta_{\alpha} \cos \theta_{\alpha}}{R^2} - \frac{\zeta_{\beta} \cos \theta_{\beta}}{R^2} - \frac{2}{R^3} \zeta_{\alpha} \zeta_{\beta} \cos \theta_{\alpha} \cos \theta_{\beta} \right. \\
&\quad \left. + \frac{\zeta_{\alpha} \zeta_{\beta} \sin \theta_{\alpha} \sin \theta_{\beta} \cos(\phi_{\beta} - \phi_{\alpha})}{R^3} \right) \quad (3.39)
\end{aligned}$$

The monopole-monopole terms collect together to give

$$- \frac{e^2}{R} \left(N_B \sum_{\alpha} Z_{\alpha} + N_A \sum_{\beta} Z_{\beta} - N_A N_B - \sum_{\alpha} \sum_{\beta} Z_{\alpha} Z_{\beta} \right)$$

$$= \frac{e^2}{R} \left(\sum_{\alpha} z_{\alpha} - N_A \right) \left(\sum_{\beta} z_{\beta} - N_B \right) \quad (3.40)$$

For a neutral molecule this vanishes because

$$\sum_{\alpha} z_{\alpha} = N_A ; \quad \sum_{\beta} z_{\beta} = N_B \quad (3.41)$$

the monopole-dipole terms also vanish, and only the dipole-dipole is left:

$$\begin{aligned} & - \{ 2N_A N_B e^2 \zeta_I \zeta_J \cos \theta_I \cos \theta_J + 2e^2 \sum_{\alpha} z_{\alpha} \zeta_{\alpha} \cos \theta_{\alpha} \sum_{\beta} \zeta_{\beta} z_{\beta} \cos \theta_{\beta} \} \frac{1}{R^3} \\ & + \frac{2e^2}{R^3} \{ N_B \zeta_J \cos \theta \sum_{\alpha} z_{\alpha} \zeta_{\alpha} \cos \theta_{\alpha} + N_A \zeta_I \cos \theta_I \sum_{\beta} z_{\beta} \zeta_{\beta} \cos \theta_{\beta} \} \\ & - \frac{e^2}{R^3} \{ N_B \zeta_J \sum_{\alpha} z_{\alpha} \zeta_{\alpha} \sin \theta_I \sin \theta_{\alpha} \cos(\phi_{\alpha} - \phi_J) + \zeta_I \sin \theta_I N_A \sum_{\beta} z_{\beta} \zeta_{\beta} \sin \theta_{\beta} \cos(\phi_{\beta} - \phi_I) \\ & + N_A N_B \zeta_I \zeta_J \sin \theta_I \sin \theta_J \cos(\phi_J - \phi_I) + \sum_{\alpha} \sum_{\beta} \zeta_{\alpha} \zeta_{\beta} \sin \theta_{\alpha} \sin \theta_{\beta} \cos(\phi_{\beta} - \phi_{\alpha}) \} \end{aligned}$$

At this point we define the molecular dipole moment operators

$$\vec{\mu}_A = -N_A e \vec{\zeta}_I + e \sum_{\alpha} z_{\alpha} \vec{\zeta}_{\alpha} \quad (3.43)$$

$$\vec{\mu}_B = -N_B e \vec{\zeta}_J + e \sum_{\beta} z_{\beta} \vec{\zeta}_{\beta} \quad (3.44)$$

It takes a little manipulation of the vectors to notice that we can write the second-order energy in terms of these dipole moment operators:-

$$\begin{aligned}
E^{(2)} = & \frac{1}{R^6} \sum_{\kappa \neq 0} \frac{1}{(E_B^0 - E_B^\kappa)} \{ \iint d^3r_I d^3r_J \rho^{00}(\vec{r}_I) \rho^{0\kappa}(\vec{r}_J) (\vec{\mu}_A \cdot \vec{\mu}_B - 3\vec{\mu}_A \cdot \hat{z} \vec{\mu}_B \cdot \hat{z}) \}^2 \\
& + \frac{1}{R^6} \sum_{\lambda \neq 0} \frac{1}{(E_A^0 - E_A^\lambda)} \{ \iint d^3r_I d^3r_J \rho^{0\lambda}(\vec{r}_I) \rho^{00}(\vec{r}_J) (\vec{\mu}_A \cdot \vec{\mu}_B - 3\vec{\mu}_A \cdot \hat{z} \vec{\mu}_B \cdot \hat{z}) \}^2 \\
& + \frac{1}{R^6} \sum_{\kappa, \lambda \neq 0} \frac{\{ \iint d^3r_I d^3r_J \rho^{0\lambda}(\vec{r}_I) \rho^{0\kappa}(\vec{r}_J) (\vec{\mu}_A \cdot \vec{\mu}_B - 3\vec{\mu}_A \cdot \hat{z} \vec{\mu}_B \cdot \hat{z}) \}^2}{(E_A^0 + E_B^0) - (E_A^\lambda + E_B^\kappa)} \\
& \dots \quad (3.45)
\end{aligned}$$

If we denote

$$\langle \vec{\mu}_A \rangle_{00} = \int d^3r_I \rho_A^{00}(\vec{r}_I) \vec{\mu}_A \quad (3.46)$$

as the expectation value of the dipole-moment operator for molecule A,

$$\text{and} \quad \langle \vec{\mu}_B \rangle_{0\kappa} = \int d^3r_J \rho_B^{0\kappa}(\vec{r}_J) \vec{\mu}_B \quad (3.47)$$

as the matrix element of the transition dipole-moment operator for molecule B, then we can write

$$\begin{aligned}
E^{(2)} = & \frac{1}{R^6} \sum_{\kappa \neq 0} \frac{\left| \langle \vec{\mu}_A \rangle_{00} \cdot \langle \vec{\mu}_B \rangle_{0\kappa} - 3 \langle \vec{\mu}_A \rangle_{00} \cdot \hat{z} \langle \vec{\mu}_B \rangle_{0\kappa} \cdot \hat{z} \right|^2}{(E_B^0 - E_B^\kappa)} \\
& + \\
& \frac{1}{R^6} \sum_{\lambda \neq 0} \frac{\left| \langle \vec{\mu}_B \rangle_{00} \cdot \langle \vec{\mu}_A \rangle_{0\lambda} - 3 \langle \vec{\mu}_B \rangle_{00} \cdot \hat{z} \langle \vec{\mu}_A \rangle_{0\lambda} \cdot \hat{z} \right|^2}{(E_A^0 - E_A^\lambda)}
\end{aligned}$$

$$\frac{1}{R^6} \sum_{\lambda, \kappa \neq 0} \left| \langle \vec{\mu}_A \rangle_{0\lambda} \cdot \langle \vec{\mu}_B \rangle_{0\kappa} - 3 \langle \vec{\mu}_A \rangle_{0\lambda} \cdot \hat{z} \langle \vec{\mu}_B \rangle_{0\kappa} \cdot \hat{z} \right|^2$$

$$(\epsilon_A^0 + \epsilon_B^0) - (\epsilon_A^\lambda + \epsilon_B^\kappa) \quad (3.48)$$

Now this form for the energy depends on the angular orientation of molecules A and B as well as the distance R. We therefore want to write down the angular average of this expression. If we let

$$\langle \vec{\mu}_A \rangle' = R(\theta_A, \phi_A, \psi_A) \langle \vec{\mu}_A \rangle \quad (3.49)$$

$$\langle \vec{\mu}_B \rangle' = R(\theta_B, \phi_B, \psi_B) \langle \vec{\mu}_B \rangle \quad (3.50)$$

be column vectors with three spatial components ($\langle \vec{\mu}_A \rangle$ and $\langle \vec{\mu}_B \rangle$ here are fixed complex vectors depending on which of the three terms are being evaluated), where θ, ϕ, ψ are the Euler angles and $R(\theta, \phi, \psi)$ is the 3×3 rotation matrix given by

$$R(\theta, \phi, \psi) = \begin{pmatrix} \cos\theta \cos\phi \cos\psi - \sin\phi \sin\psi & -\cos\theta \cos\phi \sin\psi - \sin\phi \cos\psi & -\sin\theta \cos\phi \\ \cos\theta \sin\phi \cos\psi + \cos\phi \sin\psi & -\cos\theta \sin\phi \sin\psi + \cos\phi \cos\psi & \sin\theta \sin\phi \\ -\sin\theta \cos\psi & \sin\theta \sin\psi & \cos\theta \end{pmatrix}$$

then we are left with evaluating only terms like

$$\left| \langle \vec{\mu}_A \rangle' \cdot \langle \vec{\mu}_B \rangle' - 3 \langle \vec{\mu}_A \rangle' \cdot \hat{z} \langle \vec{\mu}_B \rangle' \cdot \hat{z} \right|^2 \quad (3.52)$$

Of course we have to bear in mind that there are three "kinds" of such primed quantities as depicted by the three terms in (3.48). For simplicity, let us denote in any of the three types of terms the complex vector matrix elements by J^A and J^B . For example in the first term of 3.48,

$$\left. \begin{aligned} \langle \mu_A \rangle_{00} &\equiv \vec{J}^{A'} \\ \langle \mu_B \rangle_{0K} &\equiv \vec{J}^{B'} \end{aligned} \right\} \quad (3.53)$$

What we have done is we have rotated the (unprimed) vectors using the rotation matrix $R(\Omega_A)$ and $R(\Omega_B)$ {short for $R(\theta_A, \phi_A, \psi_A)$ and $R(\theta_B, \phi_B, \psi_B)$ respectively} containing the Euler angles. Therefore we want to evaluate

$$\begin{aligned} & \left| \vec{J}^{A'} \cdot \vec{J}^{B'} - 3 \vec{J}^{A'} \cdot \hat{z} \vec{J}^{B'} \cdot \hat{z} \right|^2 = \left| \sum_{i=1}^3 J_i^{A'} J_i^{B'} - 3 J_3^A J_3^B \right|^2 \\ &= \sum_i \sum_j J_i^{A'} J_i^{B'} J_j^{A*} J_j^{B*} - 3 \{ J_3^{A*} J_3^{B*} \sum_i J_i^{A'} J_i^{B'} + J_3^{A'} J_3^{B'} \sum_j J_j^{A*} J_j^{B*} \} \\ & \quad + 9 J_3^{A*} J_3^{A*} J_3^{B'} J_3^{B'} \end{aligned} \quad (3.54)$$

Explicitly, the complex vectors \vec{J} 's are given by

$$J_i^{A'} = \sum_k R_{ik}(\Omega_A) J_k^A \quad J_i^{B'} = \sum_k R_{ik}(\Omega_B) J_k^B \quad (3.55)$$

Thus this leads us to evaluate the angular average of the expression

$$\sum_i \sum_j \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} R_{ik}(\Omega_A) R_{j\ell}(\Omega_A) R_{i\ell'}(\Omega_B) R_{j\ell'}(\Omega_B) J_k^A J_{\ell'}^{A*} J_{\ell}^B J_{k'}^{B*}$$

$$\begin{aligned}
& - 3 \sum_i \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} R_{3\ell}(\Omega_A) R_{ik}(\Omega_A) J_\ell^A J_k^{A*} R_{3\ell'}(\Omega_B) R_{ik'}(\Omega_B) J_{\ell'}^B J_{k'}^{B*} \\
& - 3 \sum_j \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} R_{3k}(\Omega_A) R_{j\ell}(\Omega_A) J_k^A J_{\ell'}^{A*} R_{3k'}(\Omega_B) R_{j\ell'}(\Omega_B) J_{k'}^B J_{\ell'}^{B*} \\
& + 9 \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} R_{3\ell}(\Omega_A) R_{3k}(\Omega_A) J_\ell^A J_k^{A*} R_{3\ell'}(\Omega_B) R_{3k'}(\Omega_B) J_{\ell'}^B J_{k'}^{B*} \quad (3.56)
\end{aligned}$$

Now evaluating the angular average of this expression means performing integration over the Euler angles, i.e.

$$\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^\pi d\theta_A \sin\theta_A d\phi_A d\psi_A \quad \text{and} \quad \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^\pi d\theta_B \sin\theta_B d\phi_B d\psi_B \quad (3.57)$$

Now the integration of (3.56) is quite involved, but fairly straightforward. Using the result

$$\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^\pi R_{ik}(\Omega_A) R_{j\ell}(\Omega_A) d\phi_A \sin\theta_A d\theta_A d\psi_A = \frac{1}{3} \delta_{ij} \delta_{kl} \quad (3.58)$$

Our expression becomes

$$\begin{aligned}
& \sum_i \sum_j \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} \left(\frac{\delta_{ij} \delta_{kl}}{3} \right) \left(\frac{\delta_{i\ell'} \delta_{k'j}}{3} \right) J_k^A J_{\ell'}^{A*} J_{k'}^B J_{\ell'}^{B*} \\
& - 3 \sum_i \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} \left(\frac{\delta_{3i} \delta_{\ell k}}{3} \right) \left(\frac{\delta_{3i} \delta_{\ell' k'}}{3} \right) J_\ell^A J_k^{A*} J_{\ell'}^B J_{k'}^{B*} \\
& - 3 \sum_j \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} \left(\frac{\delta_{3j} \delta_{kl}}{3} \right) \left(\frac{\delta_{3j} \delta_{k' \ell'}}{3} \right) J_k^A J_{\ell'}^{A*} J_{k'}^B J_{\ell'}^{B*} \\
& + 9 \sum_\ell \sum_k \sum_{\ell'} \sum_{k'} \left(\frac{\delta_{\ell k}}{3} \right) \left(\frac{\delta_{\ell' k'}}{3} \right) J_\ell^A J_k^{A*} J_{\ell'}^B J_{k'}^{B*}
\end{aligned}$$

The action of the Kronecker deltas bring us to

$$\begin{aligned}
 & \frac{1}{9} \sum_i \sum_{\ell} \sum_{\ell'} J_{\ell}^A J_{\ell}^{A*} J_{\ell}^B J_{\ell'}^{B*} - \frac{1}{3} \sum_{\ell} \sum_{\ell'} J_{\ell}^{A*} J_{\ell}^A J_{\ell'}^{B*} J_{\ell'}^B \\
 & - \frac{1}{3} \sum_{\ell} \sum_{\ell'} J_{\ell}^{A*} J_{\ell}^A J_{\ell'}^{B*} J_{\ell'}^B + \sum_{\ell} \sum_{\ell'} J_{\ell}^A J_{\ell}^{A*} J_{\ell'}^B J_{\ell'}^{B*}
 \end{aligned} \tag{3.59}$$

We notice that the first two terms cancel because $\frac{1}{9} \sum_i 1 = \frac{1}{3}$. Thus the above expression equals

$$\begin{aligned}
 & = \frac{2}{3} (J_x^A + J_y^A + J_z^A) (J_x^B + J_y^B + J_z^B) \\
 & = \frac{2}{3} \vec{J}^A \cdot \vec{J}^A \vec{J}^B \cdot \vec{J}^B
 \end{aligned} \tag{3.60}$$

Now (3.60) is a general expression that can be used to evaluate or simplify each of the three terms in the energy expression (3.48) if we identify

$$\text{(i)} \quad \vec{J}^A = \langle \vec{\mu}_A \rangle_{00} \qquad \vec{J}^B = \langle \vec{\mu}_B \rangle_{0K} \tag{3.61a}$$

$$\text{(ii)} \quad \vec{J}^A = \langle \vec{\mu}_A \rangle_{0\lambda} \qquad \vec{J}^B = \langle \vec{\mu}_B \rangle_{00} \tag{3.61b}$$

$$\text{(iii)} \quad \vec{J}^A = \langle \vec{\mu}_A \rangle_{0\lambda} \qquad \vec{J}^B = \langle \vec{\mu}_B \rangle_{0K} \tag{3.61c}$$

With all these contributions, we can then write down the angular - average form of the second order energy as

$$\begin{aligned} \bar{E}(2) = \frac{2}{3} \frac{1}{R^6} & \left[\frac{|\langle \vec{\mu}_{A00} \rangle|^2 \sum_K |\langle \vec{\mu}_{B0K} \rangle|^2}{(E_B^O - E_B^K)} + \frac{|\langle \vec{\mu}_{B00} \rangle|^2 \sum_\lambda |\langle \vec{\mu}_{A0\lambda} \rangle|^2}{(E_A^O - E_A^\lambda)} \right. \\ & \left. + \sum_\lambda \sum_K \frac{|\langle \vec{\mu}_{A0\lambda} \rangle|^2 |\langle \vec{\mu}_{B0K} \rangle|^2}{(E_A^O + E_B^O) - (E_A^\lambda + E_B^K)} \right] \quad (3.62) \end{aligned}$$

Now we simplify this result in terms of more familiar quantities. Following the notation of Margenau and Kestner²⁵, we introduce the oscillator strengths for the corresponding electronic transition by

$$f_{OK} = \frac{2m}{3e\hbar^2} |\langle \vec{\mu}_{B0K} \rangle|^2 (E_B^K - E_B^O) \quad (3.63)$$

$$f_{O\lambda} = \frac{2m}{3e\hbar^2} |\langle \vec{\mu}_{A0\lambda} \rangle|^2 (E_A^\lambda - E_A^O) \quad (3.64)$$

where m is the electron's mass and e its charge. Rearranging, we can get the square of the magnitude of the expectation values of the dipole moment operators in terms of these oscillator strengths:-

$$|\langle \vec{\mu}_{B0K} \rangle|^2 = \frac{3e^2\hbar^2}{2m} \frac{f_{OK}}{(E_B^K - E_B^O)} \quad (3.65)$$

$$|\langle \vec{\mu}_{A0\lambda} \rangle|^2 = \frac{3e^2\hbar^2}{2m} \frac{f_{O\lambda}}{(E_A^\lambda - E_A^O)} \quad (3.66)$$

so that the second-order energy can be written as

$$\begin{aligned}
E^{(2)} = & \frac{1}{R^6} \frac{\hbar^2 e^2}{m} \left[\left| \langle \vec{\mu}_A \rangle_{00} \right|^2 \sum_{\kappa} \frac{-f_{0\kappa}}{(E_B^{\kappa} - E_B^0)^2} + \left| \langle \vec{\mu}_B \rangle_{00} \right|^2 \sum_{\lambda} \frac{-f_{0\lambda}}{(E_A^{\lambda} - E_A^0)^2} \right] \\
& + \frac{3}{2} \left\{ \frac{\hbar^2 e^2}{m} \right\}^2 \sum_{\lambda} \sum_{\kappa} \frac{f_{0\kappa} f_{0\lambda}}{(E_A^{\lambda} - E_A^0)(E_B^{\kappa} - E_B^0) - (E_A^0 + E_B^0) - (E_A^{\lambda} + E_B^{\kappa})} \\
& \dots \quad (3.67)
\end{aligned}$$

We now define the polarizability by

$$\alpha(\mu) = \frac{e^2 \hbar^2}{m} \sum_{\gamma} \frac{f_{0\gamma}}{(E_A^{\gamma} - E_A^0)^2 - \hbar^2 \mu^2} \quad (3.68)$$

where μ is a general frequency. We can have two special cases : one in which the frequency μ is generally complex, $\mu = i\omega$ where ω is real, and the other one in which the frequency μ is zero for which case we have what we call the static polarizabilities $\alpha(0)$. For example, for molecule A,

$$\alpha_A(0) = \frac{e^2 \hbar^2}{m} \sum_{\lambda} \frac{f_{0\lambda}}{(E_A^{\lambda} - E_A^0)^2} \quad (3.69)$$

For the complex frequencies, the polarizability is written as

$$\alpha_A(i\omega) \equiv \frac{e^2 \hbar^2}{m} \sum_{\lambda} \frac{f_{0\lambda}}{(E_A^{\lambda} - E_A^0)^2 + \hbar^2 \omega^2} \quad (3.70)$$

$$\alpha_B(i\omega) \equiv \frac{e^2 \hbar^2}{m} \sum_{\kappa} \frac{f_{0\kappa}}{(E_B^{\kappa} - E_B^0)^2 + \hbar^2 \omega^2} \quad (3.71)$$

We can rewrite the induction part of the spherically-averaged second order energy in terms of these "static" polarizabilities:-

$$E^{(2)} = -\frac{1}{R^6} \left(|\langle \vec{\mu}_{A00} \rangle|^2 \alpha_A(0) + |\langle \vec{\mu}_{B00} \rangle|^2 \alpha_B(0) - \frac{3}{2} \left(\frac{e\hbar^2}{m} \right)^2 \sum_{\lambda} \sum_{\kappa} \frac{f_{0\kappa} f_{0\lambda}}{(E_A^{\lambda} - E_A^0)(E_B^{\kappa} - E_B^0) \left[(E_A^0 + E_B^0) - (E_A^{\lambda} + E_B^{\kappa}) \right]} \right)$$

The third term (the dispersion energy) is still in its original form because the energy denominator is not a simple product of the two separate energy denominators. However, we can rewrite this term as an integral over the product of the frequency-dependent polarizabilities.

Claim

$$\sum_{\lambda} \sum_{\kappa} \frac{f_{0\kappa} f_{0\lambda}}{(E_A^{\lambda} - E_A^0)(E_B^{\kappa} - E_B^0) \{ (E_A^{\lambda} + E_B^{\kappa}) - (E_A^0 + E_B^0) \}} \equiv \frac{2\hbar m^2}{\pi(e\hbar)^4} \int_0^{\infty} \alpha_A(i\omega) \alpha_B(i\omega) d\omega \quad \dots (3.73)$$

Proof

Let the right-hand side of (3.73) be written out explicitly as

$$\int_0^{\infty} \alpha(i\omega) \alpha(i\omega) d\omega = \frac{(e\hbar)^4}{m^2} \sum_{\lambda} \sum_{\kappa} f_{0\lambda} f_{0\kappa} \int_0^{\infty} \frac{d\omega}{\{ (E_A^{\lambda} - E_A^0)^2 + \hbar^2 \omega^2 \} \{ (E_B^{\kappa} - E_B^0)^2 + \hbar^2 \omega^2 \}} \quad \dots (3.74)$$

If we break the integrand into partial fractions, it becomes

$$\begin{aligned}
&= \frac{(e\hbar)^4}{m^2} \sum_{\lambda} \sum_{\kappa} \frac{f_{0\kappa} f_{0\lambda}}{(E_B^{\kappa} - E_B^0)^2 - (E_A^{\lambda} - E_A^0)^2} \left[\int_0^{\infty} \frac{d\omega}{(E_A^{\lambda} - E_A^0)^2 + \hbar^2 \omega^2} - \int_0^{\infty} \frac{d\omega}{(E_B^{\kappa} - E_B^0)^2 + \hbar^2 \omega^2} \right] \\
&= \frac{(e\hbar)^4}{m^2} \sum_{\lambda} \sum_{\kappa} \frac{f_{0\kappa} f_{0\lambda}}{(E_B^{\kappa} - E_B^0)^2 - (E_A^{\lambda} - E_A^0)^2} \left[\frac{\pi}{2\hbar} \left\{ \frac{1}{(E_A^{\lambda} - E_A^0)} - \frac{1}{(E_B^{\kappa} - E_B^0)} \right\} \right] \\
&\dots (3.75)
\end{aligned}$$

Further simplifications give

$$= \frac{\pi}{2\hbar} \left(\frac{e^2 \hbar^2}{m} \right)^2 \sum_{\lambda} \sum_{\kappa} \frac{f_{0\lambda} f_{0\kappa}}{(E_A^{\lambda} - E_A^0)(E_B^{\kappa} - E_B^0) \left((E_A^{\lambda} + E_B^{\kappa}) - (E_A^0 + E_B^0) \right)} \quad (3.76)$$

Thus to within a (negative) multiplicative constant, we have shown that the claim we make in equation (3.73) is true. We can now finally write down the second-order energy correction in terms of molecular static as well as frequency-dependent polarizabilities which emerge as a dispersion integral :

$$\begin{aligned}
E^{(2)} = - \frac{1}{R^6} & \left[\left| \langle \vec{\mu}_A \rangle \right|^2 \alpha_A(0) + \left| \langle \vec{\mu}_B \rangle \right|^2 \alpha_B(0) \right. \\
& \left. + \frac{3\hbar}{\pi} \int_0^{\infty} \alpha_A(i\omega) \alpha_B(i\omega) d\omega \right] \dots (3.77)
\end{aligned}$$

In Appendix A, we show some theoretical and experimental values of the constants and parameters in this second-order Energy formula for the case of two water molecules interacting with each other²⁶.

CHAPTER IV

DERIVATION OF THE UNIVERSAL ELECTRON DENSITY AND ENERGY FUNCTIONAL

At this point let us state what we want to achieve: we would like to derive an Energy Functional - an explicit expression for an energy-like quantity as a functional of the density - such that for all densities this Energy Functional will be an upper bound to the true ground state energy whose value the functional attains at the true density ρ_0 . This Energy Functional is defined as

$$E[\rho] = \min_{\{\Psi_\rho\}} \frac{\langle \Psi_\rho | H^0 + V | \Psi_\rho \rangle}{\langle \Psi_\rho | \Psi_\rho \rangle} \quad (4.1)$$

This definition envisions obtaining $E[\rho]$ for a specified $\rho(\vec{r})$ as the minimum expectation value of the Hamiltonian after a search is made over the class of N-electron states all of which gives the same density $\rho(\vec{r})$. H^0 and V are defined in equations (3.3), (3.4) and (3.8). We can rewrite (4.1) as

$$E[\rho] = \frac{\langle \tilde{\Psi}_\rho | H^0 + V | \tilde{\Psi}_\rho \rangle}{\langle \tilde{\Psi}_\rho | \tilde{\Psi}_\rho \rangle} \quad (4.2)$$

where $|\tilde{\Psi}_\rho\rangle$ is the "optimized" wavefunction obtained as the lowest eigenstate of the following equation which follows from (2.24):-

$$\{ H^0 + V + \Lambda \} |\tilde{\Psi}_\rho\rangle = |\tilde{\Psi}_\rho\rangle \quad (4.3)$$

The Λ here which is added to the total Hamiltonian $H^0 + V$ represents an operator yet to be determined, but has a form as shown in chapter II,

$$\Lambda = \int d\vec{r} \lambda(\vec{r}) \hat{\rho}(\vec{r}) \quad (4.4)$$

where the density operator $\hat{\rho}(\vec{r})$ is the sum of one-body operators:

$$\hat{\rho}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i) \quad (4.5)$$

and $\lambda(\vec{r})$ is the Lagrange multiplier function introduced to insure the constraint $\rho(\vec{r}) = \langle \tilde{\Psi} | \hat{\rho} | \tilde{\Psi} \rangle_\rho$. $\lambda(\vec{r})$ is to be obtained in principle by inverting the expectation relation for $\rho(\vec{r})$ and get $\lambda(\vec{r}; [\rho])$.

$|\tilde{\Psi}_\rho\rangle$ is obtained as the solution of (4.3) approximately using Perturbation Theory, where the "unperturbed Hamiltonian" is H^0 while the perturbation is now $V + \Lambda$. Specifically,

$$|\tilde{\Psi}_\rho\rangle \approx |\Psi_{AB}^{00}\rangle + |\Psi^{(1)}\rangle \quad (4.6)$$

where $|\Psi^{(1)}\rangle$ is the first-order correction to the wave function and also obtained from Perturbation Theory:

$$|\Psi^{(1)}\rangle = \sum_{\lambda} \sum_{\kappa} \frac{|\Psi_{AB}^{\lambda\kappa}\rangle \langle \Psi_{AB}^{\lambda\kappa} | \epsilon V + \epsilon \Lambda | \Psi_{AB}^{00} \rangle}{E_A^0 + E_B^0 - E_A^\lambda - E_B^\kappa} \quad (4.7)$$

The ϵ is just an order parameter having value between 0 and 1 (which we will let equal 1 subsequently) whose purpose, as we shall see, is to filter out certain high orders in the final expression for $\rho(\vec{r})$.

Let us reiterate the fact about the wave functions $|\Psi_{AB}^0\rangle$ and $|\Psi_{AB}^{\lambda\kappa}\rangle$ as explained in chapter III, particularly equations (3.22) and (3.27) that since we ignore antisymmetry, the wave functions can be written as a direct product:

$$|\Psi_{AB}^0\rangle = |\Psi_A^0\rangle |\Psi_B^0\rangle \quad (4.8)$$

$$|\Psi_{AB}^{\lambda\kappa}\rangle = |\Psi_A^{\lambda}\rangle |\Psi_B^{\kappa}\rangle \quad (4.9)$$

We will now evaluate explicitly the electron density function using

$$\rho(\vec{r}) = \frac{\langle \tilde{\Psi} | \sum_i \delta(\vec{r} - \vec{r}_i) | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad (4.10)$$

The motivation for evaluating this density is so that we can obtain an expression for the Lagrange Multiplier λ in terms of ρ through inversion of this density as mentioned earlier, which in turn can be substituted into the energy (4.1) which we shall also evaluate explicitly in the forthcoming pages, so that we get the quantity that we want : that is the Energy as a functional of the density.

Now the wave function approximation (4.6) can be used to write out the denominator of (4.10) to order ϵ^2 :

$$\begin{aligned} \langle \Psi_{AB}^0 + \Psi^{(1)} | \Psi_{AB}^0 + \Psi^{(1)} \rangle &= \{ 1 + \langle \Psi^{(1)} | \Psi^{(1)} \rangle \}^{-1} \\ &\approx 1 - \langle \Psi^{(1)} | \Psi^{(1)} \rangle \end{aligned} \quad (4.11)$$

where we have used the approximation

$$(1 + \alpha)^{-1} = 1 - \alpha + \dots \quad (4.12)$$

for any α where $|\alpha| < 1$. Therefore the density is evaluated as

$$\begin{aligned} \rho(\vec{r}) = (1 - \langle \Psi^{(1)} | \Psi^{(1)} \rangle) & \left\{ \langle \Psi_A^0 \Psi_B^0 | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_A^0 \Psi_B^0 \rangle + \langle \Psi_A^0 \Psi_B^0 | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi^{(1)} \rangle \right. \\ & \left. + \langle \Psi^{(1)} | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_A^0 \Psi_B^0 \rangle + \langle \Psi^{(1)} | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi^{(1)} \rangle \right\} \\ & \dots \quad (4.13) \end{aligned}$$

It is not difficult to see that because we have neglected anti-symmetry, the first term in the curly bracket just gives the total superimposed electron density of the system :

$$\begin{aligned} \sum_i \langle \Psi_A^0 \Psi_B^0 | \delta(\vec{r} - \vec{r}_i) | \Psi_A^0 \Psi_B^0 \rangle &= \rho_{N_A}^{00}(\vec{r}) + \rho_{N_B}^{00}(\vec{r}) \\ &= \rho^{00}(\vec{r}) \quad (4.14) \end{aligned}$$

The second term gives, after a little manipulation,

$$\begin{aligned} \sum_{\lambda} \rho^{0\lambda}(\vec{r}) \left\{ \frac{\epsilon \langle V \rangle_{\lambda 0} + \epsilon \langle \Lambda \rangle_{\lambda 0}}{E_A^{\lambda} - E_A^0} \right\} &+ \sum_{\kappa} \rho^{0\kappa}(\vec{r}) \left\{ \frac{\epsilon \langle V \rangle_{\kappa 0} + \epsilon \langle \Lambda \rangle_{\kappa 0}}{E_B^{\kappa} - E_B^0} \right\} \\ &\dots \quad (4.15) \end{aligned}$$

where $\rho^{0\lambda}(\vec{r})$ and $\rho^{0\kappa}(\vec{r})$ are the "transition density" functions of the electrons in molecule A and B respectively and are defined according to

$$\rho^{0\lambda}(\vec{r}) \equiv \langle \Psi_A^0 | \hat{\rho}(\vec{r}) | \Psi_A^{\lambda} \rangle = \langle \Psi_A^0 | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_A^{\lambda} \rangle \quad (4.16)$$

$$\rho^{0K}(\vec{r}) \equiv \langle \Psi_B^0 | \rho(\vec{r}) | \Psi_B^K \rangle = \langle \Psi_B^0 | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_B^K \rangle \quad (4.17)$$

with $i \in \{1, \dots, N_A\}$ and $j \in \{N_A+1, \dots, N_A+N_B\}$. The matrix elements $\langle V \rangle_{\lambda_0}$ and $\langle \Lambda \rangle_{\lambda_0}$, for example, are short forms for

$$\langle V \rangle_{\lambda_0} = \langle \Psi_A^{\lambda} \Psi_B^0 | V | \Psi_A^0 \Psi_B^0 \rangle \quad (4.18)$$

$$\text{and} \quad \langle \Lambda \rangle_{\lambda_0} = \langle \Psi_A^{\lambda} \Psi_B^0 | \int d\vec{r} \rho(\vec{r}') \lambda(\vec{r}') | \Psi_A^0 \Psi_B^0 \rangle \quad (4.19)$$

In (4.13), the virtual excitations of both A and B molecules yield vanishing contributions since $\delta(\vec{r} - \vec{r}_i)$ is a one-body operator. When the third term in (4.13) is evaluated, it turns out that it is just the complex conjugate of (4.15):-

$$\sum_{\lambda} \rho^{\lambda_0}(\vec{r}) \left\{ \frac{\epsilon \langle V \rangle_{\lambda_0} + \epsilon \langle \Lambda \rangle_{\lambda_0}}{E_A^0 - E_A^{\lambda}} \right\} + \sum_{\kappa} \rho^{\kappa_0}(\vec{r}) \left\{ \frac{\epsilon \langle V \rangle_{\kappa_0} + \epsilon \langle \Lambda \rangle_{\kappa_0}}{E_B^0 - E_B^{\kappa}} \right\} \quad \dots \quad (4.20)$$

Evaluating the last term in (4.13) is somewhat longwinded, but there are many orthogonal terms involving terms like $\langle \Psi_A^0 | \Psi_A^{\lambda} \rangle$ and they all yield zero. Moreover, the nonvanishing terms in this expression are of order ϵ^2 which we do not really want and thus ignore. Therefore if we take only expressions of the first order ϵ (noting that $\langle \Psi^{(1)} | \Psi^{(1)} \rangle$ includes ϵ^2) and then putting $\epsilon = 1$, the density then becomes

$$\rho(\vec{r}) = \rho_A^{00}(\vec{r}) + \rho_B^{00}(\vec{r}) +$$

$$\begin{aligned}
& \sum_{\lambda} \frac{\rho^{0\lambda}(\vec{r}) < \Lambda >_{\lambda 0}}{E_A^0 - E_A^{\lambda}} + \sum_{\lambda} \frac{\rho^{\lambda 0}(\vec{r}) < \Lambda >_{\lambda 0}^*}{E_A^0 - E_A^{\lambda}} + \sum_{\kappa} \frac{\rho^{0\kappa}(\vec{r}) < \Lambda >_{\kappa 0}}{E_B^0 - E_B^{\kappa}} + \sum_{\kappa} \frac{\rho^{\kappa 0}(\vec{r}) < \Lambda >_{\kappa 0}^*}{E_B^0 - E_B^{\kappa}} \\
& + \sum_{\lambda} \frac{\rho^{0\lambda}(\vec{r}) < V >_{\lambda 0}}{E_A^0 - E_A^{\lambda}} + \sum_{\lambda} \frac{\rho^{\lambda 0}(\vec{r}) < V >_{\lambda 0}^*}{E_A^0 - E_A^{\lambda}} + \sum_{\kappa} \frac{\rho^{0\kappa}(\vec{r}) < V >_{\kappa 0}}{E_B^0 - E_B^{\kappa}} + \sum_{\kappa} \frac{\rho^{\kappa 0}(\vec{r}) < V >_{\kappa 0}^*}{E_B^0 - E_B^{\kappa}} \\
& \dots \quad (4.21)
\end{aligned}$$

Now substituting in the values for $< \Lambda >_{\lambda 0}$ and $< \Lambda >_{\kappa 0}$ which, if evaluated from (4.19) becomes

$$\begin{aligned}
< \Lambda >_{\lambda 0} &= \int d\vec{r}' (\vec{r}') < \Psi_A^{\lambda} \Psi_B^0 | \sum_i \delta(\vec{r}' - \vec{r}_i) | \Psi_A^{\lambda} \Psi_B^0 > \\
&= \int < \Psi_A^{\lambda} | \sum_i \delta(\vec{r}' - \vec{r}_i) | \Psi_A^0 > \lambda(\vec{r}) d\vec{r} \\
&= \int d\vec{r}' \rho^{\lambda 0}(\vec{r}') \lambda(\vec{r}') \quad (4.22)
\end{aligned}$$

for example, the four terms involving $< \Lambda >_{\lambda, \kappa 0}$ can be simplified as

$$\begin{aligned}
& \int d\vec{r}' \sum_{\lambda} \frac{\rho^{0\lambda}(\vec{r}) \rho^{\lambda 0}(\vec{r}')}{E_A^0 - E_A^{\lambda}} \lambda(\vec{r}') + \int d\vec{r}' \sum_{\lambda} \frac{\rho^{\lambda 0}(\vec{r}) \rho^{0\lambda}(\vec{r}')}{E_A^0 - E_A^{\lambda}} \lambda(\vec{r}') \\
& \int d\vec{r}' \sum_{\kappa} \frac{\rho^{0\kappa}(\vec{r}) \rho^{\kappa 0}(\vec{r}')}{E_B^0 - E_B^{\kappa}} \lambda(\vec{r}') + \int d\vec{r}' \sum_{\kappa} \frac{\rho^{\kappa 0}(\vec{r}) \rho^{0\kappa}(\vec{r}')}{E_B^0 - E_B^{\kappa}} \lambda(\vec{r}') \quad (4.23)
\end{aligned}$$

Let us, at this stage, define a quantity $K^{-1}(\vec{r}, \vec{r}')$ called the density-density correlation Kernel. For the molecule A, the Kernel has the form

$$\begin{aligned}
K_A^{-1}(\vec{r}, \vec{r}') &= \sum_{\lambda} \frac{\rho^{o\lambda}(\vec{r}) \rho^{\lambda o}(\vec{r}') + \rho^{o\lambda}(\vec{r}') \rho^{\lambda o}(\vec{r})}{E_A^o - E_A^{\lambda}} \\
&= 2 \operatorname{Re} \sum_{\lambda} \frac{\rho^{o\lambda}(\vec{r}) \rho^{\lambda o}(\vec{r}')}{E_A^o - E_A^{\lambda}} \quad (4.24)
\end{aligned}$$

We can also write down an analogous expression for the B molecule, and define the sum of the two Kernels as

$$K_A^{-1}(\vec{r}, \vec{r}') + K_B^{-1}(\vec{r}, \vec{r}') \equiv K^{-1}(\vec{r}, \vec{r}') \quad (4.25)$$

We shall assume the existence of the inverse Kernels K_A , K_B and K . For example, we can write

$$\int d\vec{r}'' K(\vec{r}, \vec{r}') K^{-1}(\vec{r}'', \vec{r}') = \delta(\vec{r} - \vec{r}'') \quad (4.26)$$

It is also obvious from (4.24) that by interchanging \vec{r} and \vec{r}' , the Kernel has the property

$$K^{-1}(\vec{r}, \vec{r}') = K^{-1}(\vec{r}', \vec{r}) \quad (4.27)$$

$$K(\vec{r}, \vec{r}') = K(\vec{r}', \vec{r}) \quad (4.28)$$

It should also be borne in mind that the inverse Kernels are not necessarily additive; for example

$$K_A(\vec{r}, \vec{r}') + K_B(\vec{r}, \vec{r}') \neq K(\vec{r}, \vec{r}') \quad (4.29)$$

Returning to our evaluation of the density function, writing down the transition densities in terms of the correlation-correlation Kernel offers a vast simplification to the expression of the density. We can now write $\rho(\vec{r})$ as

$$\rho(\vec{r}) = \rho^0(\vec{r}) + \rho^{(1)}(\vec{r}) + \int d\vec{r}' K^{-1}(\vec{r}, \vec{r}') \lambda(\vec{r}') + \mathcal{O}(\epsilon^2) \quad (4.30)$$

where $\rho^0(\vec{r})$ is the total superimposed electron density of the system and $\rho^{(1)}(\vec{r})$ summarizes the last four terms of (4.21) :

$$\begin{aligned} \rho^{(1)}(\vec{r}) = & \sum_{\lambda} \frac{\rho^{0\lambda}(\vec{r}) \langle V \rangle_{\lambda 0}}{E_A^0 - E_A^{\lambda}} + \sum_{\kappa} \frac{\rho^{\lambda 0}(\vec{r}) \langle V \rangle_{\lambda 0}}{E_A^0 - E_A^{\lambda}} + \\ & \sum_{\kappa} \frac{\rho^{0\kappa}(\vec{r}) \langle V \rangle_{\kappa 0}}{E_B^0 - E_B^{\kappa}} + \sum_{\kappa} \frac{\rho^{\kappa 0}(\vec{r}) \langle V \rangle_{\kappa 0}}{E_B^0 - E_B^{\kappa}} \\ & \dots \quad (4.31) \end{aligned}$$

We can also write $\rho^{(1)}(\vec{r})$ in terms of the correlation-correlation Kernel. If we write the full form for the matrix elements of V , say equation (4.18), we get

$$\begin{aligned} \langle V \rangle_{\lambda 0} = & e^2 \sum_{\beta} -Z_{\beta} \int d\vec{r}' \frac{\rho^{\lambda 0}(\vec{r}')}{|\vec{r}' - \vec{R}_{\beta}|} + e^2 \iint d\vec{r}' d\vec{r}'' \frac{\rho^{\lambda 0}(\vec{r}') \rho_B^{00}(\vec{r}'')}{|\vec{r}' - \vec{r}''|} \\ \langle V \rangle_{\kappa 0} = & e^2 \sum_{\alpha} -Z_{\alpha} \int d\vec{r}' \frac{\rho^{\kappa 0}(\vec{r}')}{|\vec{r}' - \vec{R}_{\alpha}|} + e^2 \iint d\vec{r}' d\vec{r}'' \frac{\rho^{\kappa 0}(\vec{r}') \rho_A^{00}(\vec{r}'')}{|\vec{r}' - \vec{r}''|} \\ & \dots \quad (4.32) \end{aligned}$$

In each case the orthogonality of the excited states to the ground state of the respective molecules makes two other terms vanish. And considering an almost similar expression for the complex conjugates $\langle v \rangle_{\lambda_0}^*$ and $\langle v \rangle_{\kappa_0}^*$ and substituting them into (4.31), we get

$$\begin{aligned} \rho^{(1)}(\vec{r}) = & e^2 \iint d\vec{r}' d\vec{r}'' K_A^{-1}(\vec{r}, \vec{r}') \left\{ \rho_B^{00}(\vec{r}'') - \sum_{\beta} z_{\beta} \delta(\vec{r}'' - \vec{R}_{\beta}) \right\} + \\ & \frac{e^2 \iint d\vec{r}' d\vec{r}'' K_B^{-1}(\vec{r}, \vec{r}') \left\{ \rho_A^{00}(\vec{r}'') - \sum_{\alpha} z_{\alpha} \delta(\vec{r}'' - \vec{R}_{\alpha}) \right\}}{|\vec{r}' - \vec{r}''|} \end{aligned} \quad (4.33)$$

Keeping in mind that the $\rho^{(1)}(\vec{r})$ can be written in this form involving the Kernels, we go back to our discussion on the expression for the electron density, equation (4.30). We have written $\mathcal{O}(\epsilon^2)$ to mean terms of quadratic order in ϵ , which is not quite very important in our present discussion. Let us rewrite the density as a function of \vec{r}' as

$$\rho(\vec{r}') = \rho^0(\vec{r}') + \rho^{(1)}(\vec{r}') = \int d\vec{r}'' K^{-1}(\vec{r}', \vec{r}'') \lambda(\vec{r}'') + \mathcal{O}(\epsilon^2) \quad (4.34)$$

Now if we multiply both sides of this equation by $K(\vec{r}, \vec{r}')$ and integrate over $d\vec{r}'$, the right-hand side yields

$$\iint d\vec{r}' d\vec{r}'' K(\vec{r}, \vec{r}') K^{-1}(\vec{r}', \vec{r}'') \lambda(\vec{r}'')$$

and by virtue of the property of the Kernel as explained in (4.26), this is simplified to $\lambda(\vec{r})$ through the action of the delta function. The left hand side of the equation becomes

$$\int d\vec{r}' K(\vec{r}, \vec{r}') \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \}$$

so that finally we can have an equation involving $\lambda(\vec{r})$ in terms of $\rho(\vec{r})$:

$$\lambda(\vec{r}) = \int d\vec{r}' K(\vec{r}, \vec{r}') \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \} \quad (4.35)$$

Now we want to utilize this equation in terms of the density in the derivation of the Energy Functional. The role that $\lambda(\vec{r})$ plays in this derivation will be realized shortly. Let us assert, echoing Levy and Freed, that $E[\rho]$ as a functional is merely a rule for associating a single number $E[\rho]$ with the full function $\rho(\vec{r})$. We envision evaluating

$$E[\rho] = \frac{\int d\vec{r} \int d\vec{r}' \tilde{\Psi}(\vec{r}) \left[H_A^0 + H_B^0 + \epsilon V \right] \tilde{\Psi}(\vec{r}')}{\int d\vec{r} \int d\vec{r}' \tilde{\Psi}(\vec{r}) \tilde{\Psi}(\vec{r}')} \quad (4.36)$$

$|\tilde{\Psi}_\rho\rangle$, the optimized eigenfunction as explained previously and defined in equations (4.3), (4.6) and (4.7) is obtained from Perturbation Theory. To display the role of the driving potential explicitly, let us note that (4.7) can be written as

$$|\tilde{\Psi}_\rho\rangle = |\Psi_{AB}^{00}\rangle + |\Psi^{(1,V)}\rangle + |\Psi^{(1,\Lambda)}\rangle \quad (4.37)$$

where

$$|\Psi^{(1,V)}\rangle = \sum_{\lambda} \sum_{\kappa} \frac{|\Psi_{AB}^{\lambda\kappa}\rangle \langle \Psi_{AB}^{\lambda\kappa} | V | \Psi_{AB}^{00}\rangle}{E_A^0 + E_B^0 - E_A^\lambda - E_B^\kappa} \quad (4.38)$$

$$|\Psi^{(1,\Lambda)}\rangle = \sum_{\lambda} \sum_{\kappa} \frac{|\Psi_{AB}^{\lambda\kappa}\rangle \langle \Psi_{AB}^{\lambda\kappa} | \Lambda | \Psi_{AB}^{00}\rangle}{E_A^0 + E_B^0 - E_A^\lambda - E_B^\kappa} \quad (4.39)$$

are first-order corrections to the wave functions corresponding to the potentials V and Λ . Our evaluation of the Energy Functional therefore proceeds as

$$E[\rho] = \frac{\langle \Psi_A^0 \Psi_B^0 + \Psi^{(1,V)} + \Psi^{(1,\Lambda)} | H^0 + \epsilon V | \Psi_A^0 \Psi_B^0 + \Psi^{(1,V)} + \Psi^{(1,\Lambda)} \rangle}{\langle \Psi_A^0 \Psi_B^0 + \Psi^{(1,V)} + \Psi^{(1,\Lambda)} | \Psi_A^0 \Psi_B^0 + \Psi^{(1,V)} + \Psi^{(1,\Lambda)} \rangle} \dots \quad (4.40)$$

with $H^0 = H_A^0 + H_B^0$. Expanding the denominator in Taylor series and keeping only second-order powers of the expansion, we obtain

$$E[\rho] = \{ 1 - \langle \Psi^{(1,V)} | \Psi^{(1,V)} \rangle - \langle \Psi^{(1,V)} | \Psi^{(1,\Lambda)} \rangle - \langle \Psi^{(1,\Lambda)} | \Psi^{(1,V)} \rangle - \langle \Psi^{(1,\Lambda)} | \Psi^{(1,\Lambda)} \rangle \} \times$$

$$\{ E_A^0 + E_B^0 + E^{(1)} + \langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi^{(1,V)} \rangle + \langle \Psi^{(1,V)} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle +$$

$$\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi^{(1,\Lambda)} \rangle + \langle \Psi^{(1,\Lambda)} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle + \langle \Psi^{(1,V)} | H^0 | \Psi^{(1,V)} \rangle +$$

$$\langle \Psi^{(1,\Lambda)} | H^0 | \Psi^{(1,V)} \rangle + \langle \Psi^{(1,V)} | H^0 | \Psi^{(1,\Lambda)} \rangle + \langle \Psi^{(1,\Lambda)} | H^0 | \Psi^{(1,\Lambda)} \rangle \} \dots \quad (4.41)$$

Multiplying it out and noting that the fourth and fifth terms in the Energy numerator are just the second-order energy corrections that we obtained in chapter III, we get :

$$\begin{aligned}
& E_A^0 + E_B^0 + E^{(1)} + 2\epsilon E^{(2)} + \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \\
& + \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \Lambda + \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \\
& + \sum_{\lambda \kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle (E_A^0 + E_B^0)}{(E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0)^2} + \sum_{\lambda \kappa} \Lambda \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle}{E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0} \\
& + \sum_{\lambda \kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle (E_A^0 + E_B^0)}{(E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0)^2} + \sum_{\lambda \kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2}{E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0} \\
& + \sum_{\lambda \kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2 (E_A^0 + E_B^0)}{(E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0)^2} + \sum_{\lambda \kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2}{E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0} \\
& \sum_{\lambda \kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2 (E_A^0 + E_B^0)}{(E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0)^2} - \langle \Psi^{(1,V)} | \Psi^{(1,V)} \rangle_{\{E_A^0 + E_B^0 + \mathcal{O}(\epsilon)\}} \\
& - \langle \Psi^{(1,\Lambda)} | \Psi^{(1,\Lambda)} \rangle_{\{E_A^0 + E_B^0 + \mathcal{O}(\epsilon)\}} - \langle \Psi^{(1,\Lambda)} | \Psi^{(1,V)} \rangle_{\{E_A^0 + E_B^0 + \mathcal{O}(\epsilon)\}} \\
& - \langle \Psi^{(1,V)} | \Psi^{(1,\Lambda)} \rangle_{\{E_A^0 + E_B^0 + \mathcal{O}(\epsilon)\}} \tag{4.42}
\end{aligned}$$

What we have done is this: To the third last term in the second bracket of equation (4.41) which, if written explicitly, is

$$\langle \Psi(1, \Lambda) | H_0 | \Psi(1, V) \rangle = \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \Lambda | \Psi_A^0 \Psi_B^0 \rangle (E_A^{\lambda} + E_B^{\kappa})}{(E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa})^2} \dots \quad (4.43)$$

we subtract to the numerator (i.e. to the energy term $E_A^{\lambda} + E_B^{\kappa}$) a term $(E_A^0 + E_B^0)$ so that the total factor $(E_A^{\lambda} + E_B^{\kappa} - E_A^0 - E_B^0)$ can be cancelled with one equivalent factor in the denominator. But what is subtracted is then added back and the added term materializes as the eighth term in (4.42). Doing similar addition and subtraction of terms with the other three terms involving H_0 , we obtain (4.42). Now notice that in (4.42), if we discard terms of order ϵ^3 and higher, we get a series of cancellations. The pairs that cancel are: the twelfth term with the fifteenth, the fourteenth term with the sixteenth, the eighth term with seventeenth and the tenth term with the eighteenth. We can then simplify our expression to

$$\begin{aligned} E[\rho] = & E_A + E_B + E^{(1)} + 2\epsilon E^{(2)} + \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{(E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa})} \\ & + \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} - \sum_{\lambda} \sum_{\kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \\ & - \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon V | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} + \sum_{\lambda} \sum_{\kappa} \frac{|\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle|^2}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \\ & - \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon V | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \end{aligned} \quad (4.44)$$

We see that the fifth and eighth terms cancel, as do the sixth and tenth terms. The seventh is just the second-order energy $E^{(2)}$, so it will be subtracted from the fourth term, leaving just $E^{(2)}$. Therefore our Energy Functional becomes

$$E[\rho] = E_A + E_B + E^{(1)} + E^{(2)} - \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \epsilon \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \epsilon \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \dots (4.45)$$

Now this form of the energy is not quite what we want because the functional is that of $\lambda(\vec{r})$ rather than $\rho(\vec{r})$. When we talk about energy functionals in density functional theory, we usually have in mind the expression of energy as an explicit functional of the density function (i.e. the dependence on $\rho(\vec{r})$ must not merely an implicit one, like that of equation (4.45). Therefore we want to insert the formula for $\rho(\vec{r})$ that we obtained in equation (4.35) into this energy expression. Let the summation (i.e. the fourth term in equation (4.45)) be

$$\begin{aligned} f[\lambda] &= \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \Lambda | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \Lambda | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \\ &= \iint d\vec{r} d\vec{r}' \sum_{\lambda} \sum_{\kappa} \frac{\langle \Psi_A^0 \Psi_B^0 | \sum_i \delta(\vec{r} - \vec{r}_i) \lambda(\vec{r}) | \Psi_A^{\lambda} \Psi_B^{\kappa} \rangle \langle \Psi_A^{\lambda} \Psi_B^{\kappa} | \sum_i \delta(\vec{r}' - \vec{r}_i) \lambda(\vec{r}') | \Psi_A^0 \Psi_B^0 \rangle}{E_A^0 + E_B^0 - E_A^{\lambda} - E_B^{\kappa}} \times \\ &= \iint d\vec{r} d\vec{r}' \sum_{\lambda} \frac{\rho^{0\lambda}(\vec{r}) \lambda(\vec{r}) \rho^{0\lambda}(\vec{r}') \lambda(\vec{r}')}{E_A^0 - E_A^{\lambda}} + \iint d\vec{r} d\vec{r}' \sum_{\kappa} \frac{\rho^{0\kappa}(\vec{r}) \lambda(\vec{r}) \rho^{0\kappa}(\vec{r}') \lambda(\vec{r}')}{E_B^0 - E_B^{\kappa}} \dots (4.46) \end{aligned}$$

Now using the definition of the density-density correlation kernel (4.24) this expression is simplified to

$$\begin{aligned} & \frac{1}{2} \iint d\vec{r} d\vec{r}' K_A^{-1}(\vec{r}, \vec{r}') \lambda(\vec{r}) \lambda(\vec{r}') + \frac{1}{2} \iint d\vec{r} d\vec{r}' K_B^{-1}(\vec{r}, \vec{r}') \lambda(\vec{r}) \lambda(\vec{r}') \\ &= \frac{1}{2} \iint d\vec{r} d\vec{r}' K^{-1}(\vec{r}, \vec{r}') \lambda(\vec{r}) \lambda(\vec{r}') \end{aligned} \quad (4.47)$$

Writing $\lambda(\vec{r})$ and $\lambda(\vec{r}')$ in terms of the inverted equation (4.35), we get

$$\begin{aligned} \int f[\rho] &= \frac{1}{2} \iiint d\vec{r} d\vec{r}' d\vec{r}'' d\vec{r}''' K(\vec{r}, \vec{r}'') K^{-1}(\vec{r}, \vec{r}') K(\vec{r}', \vec{r}''') \times \\ &\quad \{ \rho(\vec{r}'') - \rho^0(\vec{r}'') - \rho^{(1)}(\vec{r}'') \} \{ \rho(\vec{r}''') - \rho^0(\vec{r}''') - \rho^{(1)}(\vec{r}''') \} \\ &\quad \dots \end{aligned} \quad (4.48)$$

We can still further simplify this if we use the property of the density-density correlation Kernel (4.26) as well as the property of the Dirac delta function: $\int d\vec{r} f(\vec{r}) \delta(\vec{r} - \vec{r}') = f(\vec{r}')$. We therefore get

$$\begin{aligned} f[\rho] &= \frac{1}{2} \iint d\vec{r}'' d\vec{r}''' K(\vec{r}''', \vec{r}'') \{ \rho(\vec{r}'') - \rho^0(\vec{r}'') - \rho^{(1)}(\vec{r}'') \} \times \\ &\quad \{ \rho(\vec{r}''') - \rho^0(\vec{r}''') - \rho^{(1)}(\vec{r}''') \} \end{aligned} \quad \dots \quad (4.49)$$

Note that the \vec{r}'' and \vec{r}''' are just dummy variables and we can change them to \vec{r} and \vec{r}' . And so we get our final form of the Energy Functional:

$$E[\rho] = E_A^0 + E_B^0 + E^{(1)} + E^{(2)} - f[\rho] \quad (4.50)$$

CHAPTER V

THE GROUND-STATE ENERGY

We have now obtained, using the algorithm of Levy and Freed, an explicit expression for the Energy Functional of the system of two interacting neutral molecules in terms of a Taylor expansion in powers of $\{\rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r})\}$. Note that under the assumption that the Kernel K is negative definite, $f[\rho]$ in (4.50) is always positive so that $\rho(\vec{r})$, the optimum density which minimizes $E[\rho]$, becomes

$$\rho(\vec{r}) = \tilde{\rho}(\vec{r}) = \rho^0(\vec{r}) + \rho^{(1)}(\vec{r}) \quad (5.1)$$

Now this Energy Functional that we had obtained is the energy at a certain reference point that we called \vec{R} , the nuclear coordinates. Therefore E is parametrized by the position of the nuclei which are held fixed, and we write this as $E[\rho; \vec{R}]$. As a proper notation, let us call this fixed coordinate \vec{R}_0 instead of \vec{R} . Doing so, it is easy for us to understand that whenever we write \vec{R} , we mean a general vector position of the nuclei necessarily away from \vec{R}_0 .

Our problem now is this: we want a more general expression for the Energy Functional for points not only at \vec{R}_0 , but for other configurations in the vicinity of \vec{R}_0 . In deriving such an expression, let us start from the beginning and note that initially, we have the system's Hamiltonian to be

$$\begin{aligned}
H(\vec{R}) &= T + V_{en}(\vec{R}) + V_{ee} + V_{nn}(\vec{R}) \\
&= T + V_{en}(\vec{R}_O) + V_{ee} + V_{nn}(\vec{R}_O) + \{V_{en}(\vec{R}) - V_{en}(\vec{R}_O)\} \\
&\quad + \{V_{nn}(\vec{R}) - V_{nn}(\vec{R}_O)\}
\end{aligned} \tag{5.2}$$

where $\Delta U = V_{en}(\vec{R}) - V_{en}(\vec{R}_O)$ and $\Delta V = V_{nn}(\vec{R}) - V_{nn}(\vec{R}_O)$ and

$$V_{en}(\vec{R}_O) = \sum_k \sum_\gamma - \frac{Z_\gamma e^2}{|\vec{r}_k - \vec{R}_\gamma^O|} \tag{5.3}$$

$$V_{nn}(\vec{R}_O) = \sum_\alpha \sum_\beta \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha^O - \vec{R}_\beta^O|} \tag{5.3}$$

k is the summation index that runs over all electrons and γ is the summation index that runs over all nuclei. T is the kinetic energy operator, V_{en} the electron-nuclear interactions, V_{ee} the electron-electron repulsion and V_{nn} the nuclear-nuclear repulsion. Now calling the first four terms in (5.2) the "reference" Hamiltonian whose corresponding Energy Functional was obtained in chapter IV, we can rewrite H :

$$H(\vec{R}) = H_{ref}(\vec{R}_O) + \Delta U + \Delta V \tag{5.4}$$

Explicitly, $H_{ref}(\vec{R}_O)$ is the Hamiltonian on which we have been working in chapter IV, namely

$$\begin{aligned}
H_{ref}(\vec{R}_O) &= T_A + V_{en}^A(\vec{R}_O) + V_{ee}^A + V_{nn}^A(\vec{R}_O) \\
&\quad + T_B + V_{en}^B(\vec{R}_O) + V_{ee}^B + V_{nn}^B(\vec{R}_O)
\end{aligned} \tag{5.5}$$

with the corresponding (eigenvalue) Energy Functional

$$E_{\text{ref}}[\rho; \vec{R}_O] = E_A^0 + E_B^0 + E^{(1)}(\vec{R}_O) + E^{(2)}(\vec{R}) - f[\rho; \vec{R}_O] \quad (5.6)$$

where $f[\rho; \vec{R}_O]$ is equation (4.49) of chapter IV and is the functional of the density arising from the constraint. Specifically,

$$f[\rho; \vec{R}_O] = \frac{1}{2} \iint d\vec{r} d\vec{r}' K(\vec{r}, \vec{r}') \{ \rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) \} \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \}$$

It should be borne in mind that the Kernel K is parametrized by \vec{R}_O through its dependence on the transition densities.

Therefore the total Energy Functional in the whole configuration of the potential energy surface is given by

$$\begin{aligned} E[\rho; \vec{R}] &= \min_{\{|\Psi\rangle\}} \{ \langle \Psi | H_{\text{ref}}(\vec{R}_O) + \Delta U + \Delta V | \Psi \rangle \} \\ &= \min_{\{|\Psi\rangle\}} \{ \langle \Psi | H_{\text{ref}}(\vec{R}_O) | \Psi \rangle \} + \int d\vec{r} \tilde{\Delta U} \rho(\vec{r}) + \Delta V \end{aligned} \quad (5.8)$$

We should note that the integral involving $\tilde{\Delta U}$ can be removed from the minimization search because it depends only of ρ and not $|\Psi\rangle$.

ΔV is constant throughout. Thus $E[\rho; \vec{R}]$ can be written as

$$E[\rho; \vec{R}] = E_{\text{ref}}[\rho; \vec{R}_O] + E_U[\rho; \vec{R}, \vec{R}_O] + \Delta V \quad (5.9)$$

a where $E_U[\rho; \vec{R}, \vec{R}_O] = \int d\vec{r} \rho(\vec{r}) \tilde{\Delta U}$ and $\tilde{\Delta U}$ is a prototype of

$$\Delta U = \sum_k \sum_Y \frac{-Z_Y e^2}{|\vec{r}_k - \vec{R}_Y|} - \sum_k \sum_Y \frac{-Z_Y e^2}{|\vec{r}_k - \vec{R}_Y^0|}$$

If we define the auxilliary functional

$$F[\rho] = E[\rho] - \mu \left\{ \int \rho(\vec{r}) d\vec{r} - N \right\} \quad (5.10)$$

then the problem of extremizing the functional,

$$\delta F[\rho] = 0 \quad (5.11)$$

involves evaluating the variation in F :

$$F[\rho + \delta\rho] - F[\rho] = \int d\vec{r} \left\{ \frac{\delta F}{\delta\rho} \right\} \delta\rho + \mathcal{O} \left[\left\{ \frac{\delta\rho}{\rho} \right\}^2 \right] = 0 \quad (5.12)$$

which defines the functional derivative $\frac{\delta F}{\delta\rho}$. Using (5.10), and then writing the forms of the energy explicitly, we obtain for $F[\rho + \delta\rho]$:

$$\begin{aligned} F[\rho + \delta\rho] &= E_{\text{ref}}[\rho + \delta\rho] + E_{\text{U}}[\rho + \delta\rho] - \mu \left\{ \int d\vec{r} [\rho + \delta\rho] - N \right\} \\ &= E_A + E_B + E^{(1)}(\vec{R}_0) + E^{(2)}(\vec{R}_0) \\ &\quad - \frac{1}{2} \iint d\vec{r} d\vec{r}' \{ \rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) + \delta\rho(\vec{r}) \} K(\vec{r}, \vec{r}') \times \\ &\quad \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') + \delta\rho(\vec{r}') \} \\ &\quad + \int d\vec{r} \{ \rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) + \delta\rho(\vec{r}) \} \Delta U(\vec{r}) \\ &\quad - \mu \left\{ \int d\vec{r} [\rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) + \delta\rho(\vec{r})] - N \right\} \quad (5.13) \end{aligned}$$

$$\begin{aligned}
F[\rho] &= E_A^0 + E_B^0 + E^{(1)}(\vec{R}_0) + E^{(1)}(\vec{R}_0) + \Delta V \\
&- \frac{1}{2} \iint d\vec{r} d\vec{r}' K(\vec{r}, \vec{r}') \{ \rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) \} \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \} \\
&- \int d\vec{r} \rho(\vec{r}) \Delta U(\vec{r}) - \mu \{ \int d\vec{r} \rho(\vec{r}) - N \}
\end{aligned} \tag{5.14}$$

Now we know that for the optimum density $\tilde{\rho}$,

$$F[\tilde{\rho} + \delta\rho] - F[\tilde{\rho}] = 0 \tag{5.15}$$

Subtracting the two expressions that we obtained above, we get

$$\begin{aligned}
0 &= - \frac{1}{2} \iint d\vec{r} d\vec{r}' \{ \tilde{\rho}(\vec{r}) \tilde{\rho}(\vec{r}') + \tilde{\rho}(\vec{r}) \delta\rho(\vec{r}') - \tilde{\rho}(\vec{r}) \delta\rho(\vec{r}') - \tilde{\rho}(\vec{r}) \rho^{(1)}(\vec{r}') \\
&+ \delta\rho(\vec{r}) \tilde{\rho}(\vec{r}') + \delta\rho(\vec{r}) \delta\rho(\vec{r}') - \delta\rho(\vec{r}) \rho_0(\vec{r}') - \delta\rho(\vec{r}) \rho^{(1)}(\vec{r}') \\
&- \rho_0(\vec{r}) \tilde{\rho}(\vec{r}') - \rho_0(\vec{r}) \delta\rho(\vec{r}') + \rho_0(\vec{r}) \rho_0(\vec{r}') + \rho_0(\vec{r}) \rho^{(1)}(\vec{r}') \\
&- \rho^{(1)}(\vec{r}) \rho(\vec{r}') - \rho^{(1)}(\vec{r}) \delta\rho(\vec{r}') + \rho^{(1)}(\vec{r}) \rho_0(\vec{r}') + \\
&+ \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \} K(\vec{r}, \vec{r}') + \int d\vec{r} \{ \tilde{\rho}(\vec{r}) \Delta U(\vec{r}) \} - \\
&\left\{ \int d\vec{r} \delta\rho(\vec{r}) \Delta U(\vec{r}) - \mu \{ \int d\vec{r} \tilde{\rho}(\vec{r}) + \int d\vec{r} \delta\rho(\vec{r}) - N \} \right. \\
&+ \frac{1}{2} \iint d\vec{r} d\vec{r}' \{ \tilde{\rho}(\vec{r}) \tilde{\rho}(\vec{r}') - \tilde{\rho}(\vec{r}) \rho_0(\vec{r}') - \tilde{\rho}(\vec{r}) \rho^{(1)}(\vec{r}') - \rho_0(\vec{r}) \tilde{\rho}(\vec{r}') \\
&+ \rho_0(\vec{r}) \rho_0(\vec{r}') + \rho_0(\vec{r}) \rho^{(1)}(\vec{r}') - \rho^{(1)}(\vec{r}) \tilde{\rho}(\vec{r}') + \rho^{(1)}(\vec{r}) \rho_0(\vec{r}') \\
&+ \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \} K(\vec{r}, \vec{r}') - \int d\vec{r} \tilde{\rho}(\vec{r}) \Delta U(\vec{r}) + \\
&\left. + \mu \left[\int d\vec{r} \{ \tilde{\rho}(\vec{r}) - \delta\rho(\vec{r}) \} - N \right] \right\}
\end{aligned} \tag{5.16}$$

After a series of cancellations, and discarding quadratic and higher orders in $\delta\rho$, plus using the symmetric property of the Kernel:

$$K(\vec{r}, \vec{r}') = K(\vec{r}', \vec{r}) \quad (5.17)$$

our expression is reduced to

$$\begin{aligned} & - \int d\vec{r} d\vec{r}' \delta\rho(\vec{r}') \left[\rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) \right] K(\vec{r}, \vec{r}') \\ & - \int \{ \delta\rho(\vec{r}) \Delta U(\vec{r}) - \mu \int \delta\rho(\vec{r}) \} d\vec{r} = 0 \end{aligned} \quad (5.18)$$

Now if we rearrange this equation so that

$$\begin{aligned} & \int d\vec{r} \delta\rho(\vec{r}) \left\{ \int d\vec{r}' \left[\rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \right] K(\vec{r}, \vec{r}') \right. \\ & \left. + \Delta U(\vec{r}) - \mu \right\} = 0 \end{aligned} \quad (5.19)$$

we can clearly see that due to the fact that $\delta\rho(\vec{r})$ is an arbitrary variation, then the integrand in the integral is zero, giving

$$- \int d\vec{r}' \{ \rho(\vec{r}') - \rho^0(\vec{r}') - \rho^{(1)}(\vec{r}') \} K(\vec{r}, \vec{r}') = \mu - \Delta U(\vec{r}) \quad (5.20)$$

Multiplying both sides by $K^{-1}(\vec{r}, \vec{r}')$ and integrating over $d\vec{r}$, and using the property of the Kernel (4.26) as well as the dirac delta function, we get

$$\rho(\vec{r}) - \rho^0(\vec{r}) - \rho^{(1)}(\vec{r}) = - \int d\vec{r}' K^{-1}(\vec{r}, \vec{r}') \{ \mu - \Delta U(\vec{r}') \} \quad (5.21)$$

where we have taken into account the fact that all the variables in the integrals are just dummy variables so that \vec{r}' can be interchanged to \vec{r} and so on. Now on the right hand side of (5.21) we have an integral of an operator $K^{-1}(\vec{r}, \vec{r}')$ operating on a function involving a constant μ and a position-dependent potential $\Delta U(\vec{r}')$. But

$$\int K^{-1}(\vec{r}, \vec{r}') \mu \, d\vec{r}' = 0 \quad (5.22)$$

because the integral involves expressions like

$$\int \langle \Psi_A^\lambda | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_A^0 \rangle = N_A \langle \Psi_A^\lambda | \Psi_A^0 \rangle \quad (5.23)$$

which is zero due to the orthogonal property of the wave functions.

We therefore have now obtained the optimum density $\tilde{\rho}(\vec{r})$. From (5.21), it can be written as

$$\tilde{\rho}(\vec{r}) = \rho^0(\vec{r}) + \rho^{(1)}(\vec{r}) + \int d\vec{r}' K^{-1}(\vec{r}, \vec{r}') \Delta U(\vec{r}') \quad (5.24)$$

According to the Hohenberg-Kohn theorem, this is the density that will produce the ground state energy of the system if it is used as the density in the Energy Functional (5.8). Of course, this is within the context of approximation to the functional itself. Substituting this form for the optimum density into (5.8), we get

$$E[\rho] = E_A^0 + E_B^0 + E^{(1)}(\vec{R}_O) + E^{(2)}(\vec{R}_O) + \Delta V$$

$$-\frac{1}{2} \iint d\vec{r} d\vec{r}' K(\vec{r}', \vec{r}) \left\{ \int d\vec{r}'' K^{-1}(\vec{r}', \vec{r}'') \Delta U(\vec{r}'') \right\} K \left\{ \int d\vec{r}''' K^{-1}(\vec{r}, \vec{r}''') \Delta U(\vec{r}''') \right\}$$

$$+ \int \rho_0(\vec{r}'') \Delta U(\vec{r}'') d\vec{r}'' + \int \rho^{(1)}(\vec{r}'') \Delta U(\vec{r}'') d\vec{r}'' + \int d\vec{r}' d\vec{r}'' K^{-1}(\vec{r}'', \vec{r}') \Delta U(\vec{r}') \Delta U(\vec{r}'') \quad (5.25)$$

The sixth term can be simplified using the property of the Kernel, equation (4.26) as well as the Dirac Delta function. Since all integration variables are dummy variables, we can change them into \vec{r} and \vec{r}' . Our final expression for the energy becomes

$$E[\rho] = E_A^0 + E_B^0 + E^{(1)}(\vec{R}_0) + E^{(2)}(\vec{R}_0) + \frac{1}{2} \iint d\vec{r} d\vec{r}' \Delta U(\vec{r}) K^{-1}(\vec{r}, \vec{r}') \Delta U(\vec{r}') + \int \rho_0(\vec{r}) \Delta U(\vec{r}) d\vec{r} + \int \rho^{(1)} \Delta U(\vec{r}) d\vec{r} \quad (5.26)$$

Thus have we obtained the Ground-State Energy of the system of two interacting molecules using the Energy Functional derived in chapter IV valid only for long-range forces acting between them using a method which does not take into account the explicit form of the system's wave functions as in the traditional quantum-mechanical formalism. Equipped with the expression for the electron density which we derived and then finding the Energy as a functional of this density, we applied the variational procedure to this Energy Functional to get the "optimum" density which, according to the Hohenberg-Kohn theorem, will produce the Ground-State Energy when substituted into the Energy Functional.

What is unclear at this juncture, and perhaps something worth investigating into in the future, is whether the theory is valid for short-range forces; i.e. at distances which are not far away from \vec{R}_0 . Remember that the Energy Functional "at" \vec{R}_0 which we called $E_{\text{ref}}[\rho; \vec{R}_0]$ is not exact and its derivation involves some approximations. Thus we

simply cannot extrapolate the use of the Energy Functional and the Ground-State Energy to include short-range forces.

Nevertheless, we hope that the simplicity of the method of Density Functional Theory as well as the vast simplification it suggests to the computational aspects will make this formulation a standard method for evaluating Ground-State Energies of atomic and molecular systems in the future.

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Appendix A

Dispersion Energy Constants and Dipole Polarizabilities for the Water-Water Interaction.

Quantity	Theoretical	Experimental
$C_6(\text{H}_2\text{O})$	$47.3 \pm 5.5 \text{ hartree (bohr)}^6$	$45.37 \text{ hartree (bohr)}^6$
$\alpha(\text{O})$	9.86 bohr^3	9.642 bohr^3

$C_6(\text{H}_2\text{O})$ - The orientation-averaged long-range dipole-dipole dispersion dispersion energy coefficient for the water-water interaction, which is the third term in the bracket in equation (3.77)

$\alpha(\text{O})$ - The dipole polarizability for one water molecule

2
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